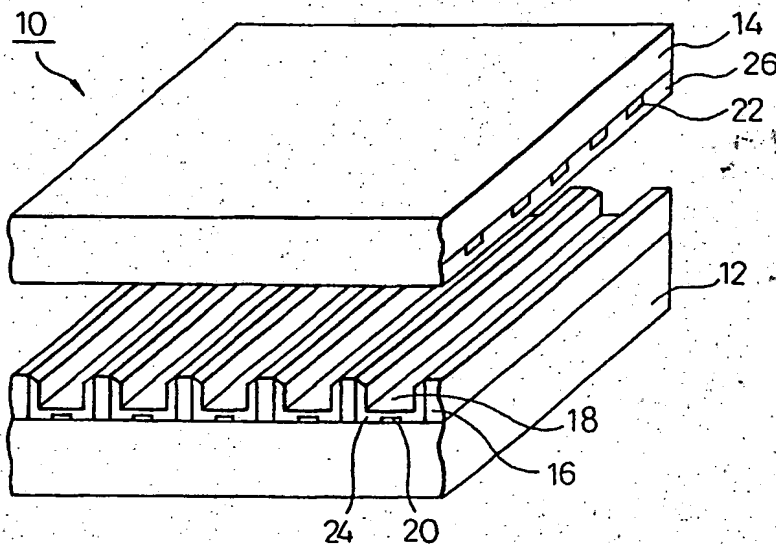


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(21) International Application Number: PCT/US00/03953 (22) International Filing Date: 16 February 2000 (16.02.00) (30) Priority Data: 11/82003 25 March 1999 (25.03.99) JP (71) Applicant (for all designated States except US): MINNESOTA MINING AND MANUFACTURING COMPANY [US/US]; 3M Center, P.O. Box 33427, Saint Paul, MN 55133-3427 (US). (72) Inventor; and (75) Inventor/Applicant (for US only): YOKOYAMA, Chikafumi [JP/JP]; 5-12-41-102, Suge, Tamaku, Kawasaki-shi, Kanagawa 214-0001 (JP). (74) Agents: PECHMAN, Robert, J. et al.; Minnesota Mining and Manufacturing Company, Office of Intellectual Property Counsel, P.O. Box 33427, Saint Paul, MN 55133-3427 (US).		(81) Designated States: AE, AL, AM, AT, AT (Utility model), AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, CZ (Utility model), DE, DE (Utility model), DK, DK (Utility model), DM, EE, EE (Utility model), ES, FI, FI (Utility model), GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KR (Utility model), KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SK (Utility model), SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>

(54) Title: METHOD OF PRODUCING SUBSTRATE FOR PLASMA DISPLAY PANEL AND MOLD USED IN THE METHOD

**(57) Abstract**

A method of producing a substrate for a plasma display panel by providing a rib on a base, which comprises the steps of contacting a rib precursor containing a first photo-setting initiator having a first absorption edge and a first photo-setting component closely with said base; filling a mold, obtained by photo-setting of a second photo-setting initiator having a second absorption edge whose wavelength is shorter than a wavelength corresponding to said first absorption edge of said first photo-setting initiator, with said rib precursor; exposing said rib precursor to light having a wavelength longer than a wavelength corresponding to said second absorption edge, thereby setting said rib precursor; and removing said mold.

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METHOD OF PRODUCING SUBSTRATE FOR PLASMA DISPLAY PANEL AND MOLD USED IN THE METHOD

5 The present invention relates to a method of producing a substrate for a plasma display panel (hereinafter also referred to as "PDP") and a mold used in the method.

Background

10 PDP is expected to be used as a thin large-image display device. Generally, PDP is equipped with a so-called substrate for PDP. Typical substrate for PDP is composed of a pair of glass flat plates facing each other at a distance via a rib having a predetermined dimension (also referred to as a barrier rib, partition or barrier). In this case, such a rib separates space between a pair of glass plates into cells in an air-tight manner to form a plurality of discharge display cells capable of containing a discharge gas such as neon, helium or xenone.

15 Various suggestions have been made to produce and provide the rib and, for example, a method of using a mold is known. Generally, according to this method, a molding material is filled up in the mold and is converted into a molded article capable of transferring to a plate-shaped base by a thermal or optical action. On removing the mold from the rib, the rib is produced and provided, nearly continuously, with comparatively high accuracy.

20 In the case of a general substrate for PDP, for example, a base made of glass or ceramic and a rib are used. On the other hand, a mold for a typical substrate for PDP is made of a metal, glass or ceramic as disclosed, for example, in Unexamined Patent Publication (KOKAI) No. 9-12336. Accordingly, the base and rib have almost the same hardness as or lower than that of the mold. As a result, when the mold is removed from the rib, there is a fear of causing breakage of the base or rib, or breakage of the mold itself. Such severe breakage often occurs when the rib is press-molded by using a mold made of glass, ceramic or metal as disclosed in Unexamined Patent Publication (KOKAI) No. 9-283017. The mold is repeatedly used for mass production. It is not preferred to leave the broken rib in the mold, since it is necessary to wash the mold every time the rib is made, thereby lowering the productivity.

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Unexamined Patent Publication (KOKAI) No. 9-134676 also discloses that a mold made of a silicone resin having a hardness lower than that of glass or ceramic is used. However, the silicone resin is generally brittle. Accordingly, it cannot be expected to repeatedly use the mold made of the silicone resin for mass production.

Summary of the Invention

It is an object of the present invention to provide a method of producing a substrate for PDP, capable of repeatedly using a mold with avoiding breakage of a base or a rib, and a mold used in the same.

According to the present invention, there is provided a method of producing a substrate for a plasma display panel by providing a rib on a base, which comprises the steps of:

contacting a rib precursor containing a first photo-setting initiator having a first absorption edge and a first photo-setting component closely with said base;

filling a mold, obtained by photo-setting of a second photo-setting initiator having a second absorption edge whose wavelength is shorter than a wavelength corresponding to said first absorption edge of said first photo-setting initiator, with said rib precursor;

exposing said rib precursor to light having a wavelength longer than a wavelength corresponding to said second absorption edge, thereby setting said rib precursor; and removing said mold.

The term "absorption edge", used in the present specification refers to a wavelength portion wherein an absorbency in a continuous light absorption spectrum of an object drastically decreases and it becomes transparent when the wavelength becomes longer than said wavelength portion.

According to the present invention, there is also provided a mold for a substrate for a plasma display panel comprising a base and a rib formed from a rib precursor containing a first photo-setting initiator having a first absorption edge and a first photo-setting component, said mold being obtained by photo-setting a second photo-setting component in the presence of a second photo-setting initiator having an absorption edge whose wavelength is shorter than a wavelength corresponding to said first absorption edge of said first photo-setting initiator.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a partially exploded perspective view showing one embodiment of the substrate for PDP.

Fig. 2 is a flow sheet showing the steps of the method of producing the substrate for PDP according to the present invention.

Detailed Description

The present invention will be described by way of the following embodiments but is not limited thereto, as is apparent to a person with ordinary skill. In the drawings, the same reference numeral is applied to the same or equivalent portion.

In a partially exploded perspective view of Fig. 1, one embodiment of the substrate for PDP according to the present invention is schematically shown. This substrate 10 for PDP is used so-called A.C. PDP and is preferably equipped with transparent flat plates made of easily available soda-lime glass, which are facing each other at a distance, i.e. a back plate 12 and a front plate 14. Between the back plate 12 and front plate 14, plural ribs 16 having a predetermined dimension are provided to separate the space between the plates into cells, thereby making it possible to form a plurality of discharge display cells 18.

The rib 16 shown in the figure is formed from a photosensitive paste (rib precursor). Preferable photosensitive paste contains a first photo-setting component as a binder component, a photo-setting initiator having a first absorption edge and a ceramic powder and, if necessary, a glass powder. The ceramic powder is used for affording a fixed shape to the rib, and is preferably made of alumina, silica, titania or wollastonite having high strength.

The first photo-setting component is photopolymerized in the presence of the photo-setting initiator having a first absorption edge, thereby making it possible to retain the shape of the rib 16. The first photo-setting component is not specifically limited, but is preferably an acrylic resin. For example, the first photo-setting component may also be made from an acrylic monomer or oligomer, or a silane coupling agent having a methacryl group. Specifically, HEMA (hydroxyethyl methacrylate), HEA (hydroxyethyl acrylate), Bis GMA (bis-phenol A diglycidylether methacrylate) or triethylene glycol dimethacrylate monomer or oligomer thereof etc. can be preferably used.

Particularly, when the first photo-setting component is made of a silane coupling agent having a methacryl group, a network is formed by photopolymerization of the methacryl group, thereby making it possible to retain and contain the ceramic powder. In addition, the first photo-setting component of the silane coupling agent forms polymeric silicon dioxide having a high melting point by calcination. This network due to the silane coupling agent is substantially retained by silicon dioxide even at comparatively high temperature after calcination, thereby making it possible to retain the ceramic powder or glass powder. Such a silane coupling agent is preferably γ -methacryloxypropylmethyltrimethoxysilane, γ -methacryloxypropylmethyldimethoxysilane, γ -methacryloxypropyltriethoxysilane or γ -methacryloxypropylmethyldiethoxysilane having a molecular weight of 232 to 290 in view of availability.

The glass powder is used to enhance the strength by affording a dense structure to the rib. Basically, the glass powder is used in the amount enough to fill up small space between the network made of silicon dioxide and the ceramic powder surrounded with the network. When the network does not exist, it is not necessary that the glass powder does not fill up large space between ceramic powders. As a result, the strength of the rib can be increased by a comparatively small amount of the glass powder. For example, even if the glass powder exclusively contains lead having high mass adsorption coefficient, the rate of photo-setting is hardly influenced. Use of the glass powder made of expensive glass having a low melting point can also be inhibited. Basically, the glass powder is contained in the amount of 10 to 70% by volume. Preferably, the glass powder is contained in the amount of 20 to 50% by volume, thereby further increasing the strength of the rib.

When this network is heated, together with the glass powder, the network is retained as far as silicon dioxide constituting it does not reach the melting point of silicon dioxide, thereby to cause no change in volume, substantially. If any change in volume arises, the degree is small.

When the front plate 14 or back plate 12 is, for example, made of glass having an annealing point of 550°C, the glass powder preferably has a softening point of 450 - 550°C lower than the annealing point of the plates. Even if the glass powder having such a softening point is heated together with the front plate or back plate of glass to flow into a gap, a thermal deformation of the front plate 14 or back plate 12 can be prevented. The

glass powder is made of lead glass containing boron, zinc, phosphoric acid, lead, titanium or a combination thereof, aluminum phosphate glass, boron-titanium glass, bismuth glass or zinc glass. In order to reduce the time of photo-setting of the rib precursor without taking high mass absorption coefficient into consideration, boron, zinc, phosphoric acid, titanium or a combination thereof is preferably contained. In this case, each composition is not specifically limited.

In each discharge display cell 18, an address electrode 20 is provided on a back plate 12 along a rib 16. On a front plate 14, a transparent bus electrode 22 made of an indium tin oxide (ITO) is provided vertically to the rib 16. In addition, a discharge gas such as neon, helium, xenone or the like is contained between the address electrode 20 and bus electrode 22, thereby making it possible to emit light by discharge. On each address electrode 20, a fluorescent layer 24 is provided in a predetermined order, thereby making it possible to perform color display. On the front plate 14 and bus electrode 22, a transparent dielectric layer 26 is provided to coat the bus electrode 22, thereby making it possible to extend life of PDP by inhibition of sputtering of the bus electrode 22.

With reference to a flow sheet showing the steps of the production of the substrate for PDP shown in Fig. 2, formation of a rib and an apparatus therefor will be described in detail below.

First, a mold 30 having a concave portion 28 corresponding to the shape of a rib 16 is prepared (see Fig. 2(A)). Not shown in the drawing, the concave portion 28 may have a section in the shape of trapezoid. Also not shown in the drawing, releasability may also be imparted to the mold by coating the surface of the concave portion with a releasing agent.

This mold 30 can be obtained by photo-setting of a second photo-setting component in the presence of a second photo-setting initiator having a second absorption edge. As the second photo-setting component, an acrylic monomer or oligomer can be used. Specifically, as an acrylic monomer or oligomer, an aliphatic urethane acrylate, commercially available from Henschel Co. in the tradename of "Photomer 6010", or 1,6-hexanediol diacrylate commercially available from Shin-Nakamura Chemical Co. can be preferably used. Since the mold is molded by photopolymerization, cutting of the resulting mold 30 is not required. Since photopolymerization proceeds comparatively quickly, the mold 30 can be easily obtained in a short time.

Since such a mold 30 has a hardness lower than that of general glass or ceramic, breakage of the rib and base can be avoided in case of removing the mold from the substrate. As a result, the mold can be repeatedly used without being washed.

As mentioned above, photopolymerization of the second photo-setting component is conducted in the presence of the second photo-setting initiator having a second absorption edge whose wavelength is shorter than a wavelength corresponding to the second absorption edge of the first photo-setting initiator. Such a second photo-setting initiator cannot absorb light whose wavelength is longer than a wavelength corresponding to the second absorption edge. On the other hand, when the rib precursor is set by light having a wavelength longer than a wavelength corresponding to the second absorption edge, only the first photo-setting component is set by photopolymerization, thereby making it possible to avoid simultaneous photopolymerization of the second photo-setting component, even if unreacted second photo-setting component is remained in the mold 30. Preferable photo-setting initiator includes, for example, aminoketones (400 - 430 nm), bisacylphosphine oxide (440 nm), camphorquinone (500 nm), metallocene hydroxyketone (500 nm) and benzyl dimethyl ketal (380 nm), and are commercially available from Ciba Geigy Co. under the trade name of Irgacure 2959 (370 nm), Irgacure 184 (380 nm), Dalocure 1173 (380 nm), Irgacure 500 (380 nm), Irgacure 1000 (380 nm), Irgacure 651 (390 nm), Irgacure 907 (400 nm), Irgacure 149 (420 nm), Irgacure 1700 (440 nm), Irgacure 1850 (440 nm), Irgacure 819 (450 nm), Irgacure 369 (480 nm) and Irgacure 784 (500 nm). Accordingly, selection of the first photo-setting initiator and the second photo-setting initiator can be done by appropriately select two kinds of photo-setting initiators having different absorption edges listed above. A combination of the first photo-setting initiator and second photo-setting initiator includes, for example, Dalocure 1173 having an absorption edge at a wavelength corresponding to 380 nm and Irgacure 819 having an absorption edge at a wavelength corresponding to 440 - 450 nm, Irgacure 1700 and Irgacure 1850, or the like.

Then, a photosensitive paste 32 is applied on the mold 30 and the concave portion 28 is filled with it (see Fig. 2(B)). The photosensitive paste 32 preferably has a viscosity of 1×10^3 to 1×10^5 cps. By using the viscosity within such a range, filling up of the photosensitive paste can be conducted with high accuracy. The photosensitive paste

containing a silane coupling agent as the first photo-setting component may contain a mineral acid such as hydrochloric acid, nitric acid or the like to hydrolyze the silane coupling agent, thereby providing a photosensitive paste in the form of a sol. Such a photosensitive paste is not gelled by drying, thereby making it possible to disperse the ceramic powder and ceramic powder. Furthermore, the viscosity does not depend on the amount of water.

Then, a back plate 12 is made contact with the photosensitive paste 32 (see Fig. 2(C)). The second photo-setting component mentioned above can impart flexibility to the mold 30 on photopolymerization. In such case, the mold 30 is made contact with the photosensitive paste 32 from one end by bending the mold. Accordingly, an air between the back plate 12 and the photosensitive paste 32 is efficiently removed out to the exterior and infiltration of the air into the photosensitive paste 32 is also avoided.

Then, the first photo-setting component is polymerized by exposing the photosensitive paste 32 to light (hv) having a wavelength longer than that of the second absorption edge of the second photo-setting component, thereby obtaining a rib molded article 34 (see Fig. 2(C)). In this case, the polymerization is basically conducted only by light exposure and does not require heat management whose control is difficult, in principle. The second photo-setting component of the present embodiment can also impart transparency to the mold 30 on photopolymerization. When the mold 30 is transparent, exposure of the photosensitive paste 30 to light can be conducted simultaneously from both surfaces through not only the back plate 12 but also through the mold 30. As a result, light can sufficiently reach the first photo-setting initiator and first photo-setting component, which exist in the depths of the concave portion 28, and the unreacted first photo-setting component is not remained at the free end of the molded article 34. Furthermore, substantially uniform mechanical strength is afforded to the molded article 34.

Light used for exposure has a comparatively long wavelength and is absorbed only in the first photo-setting initiator. Therefore, light is not substantially absorbed by the second photo-setting initiator, and only the polymerization of the first photo-setting component is initiated to obtain the molded article 34. As a result, even if the unreacted second photo-setting component is remained in the mold 30, it is possible to inhibit the unreacted second photo-setting component from reacting with the first photo-setting

component. That is, the molded article 34 is capable of avoiding adhesion to the mold 30 by photopolymerization.

Then, the molded article 34 is removed from the mold 30, thereby transferring the molded article 34 integrally to the back plate (see Fig. 2(D)). As mentioned above, adhesion of the molded article 34 to the mold is avoided. Accordingly, such a removal can be easily conducted without causing breakage of the back plate 12 or molded article 34 or its free end, thereby to leave it in the mold 30. As a result, it becomes possible to repeatedly use the mold 30 without being washed, thereby making it possible to improve the productivity of the substrate for PDP.

Then, both of the molded article 34 and back plate 12 are put in a calcining oven (not shown) and calcined at a predetermined temperature to obtain a rib 16 (see Fig. 2(E)). Before and after this calcination, retention of the network mentioned above is substantially made, thereby reducing shrinkage of the molded article. Accordingly, it is possible to make a rib corresponding to the shape of the concave portion with good accuracy.

If necessary, an address electrode may also be formed between ribs on the back plate, and fluorescent layer may be provided on the address electrode. Then, a transparent front plate, on which a bus electrode has previously been formed, may also be disposed to face with the back plate via a rib. Furthermore, the peripheral portions of the front plate and back plate may be sealed in an air-tight manner by using a sealing material which is not shown in the drawing, thereby forming a discharge display cell between the front plate and back plate. Thereafter, the discharge display cell may be evacuated and a discharge gas may be introduced to form a substrate for PDP.

Although the present invention has been described in accordance with the a.c. substrate for PDP, it is understood by a person with ordinary skill that the present invention can also be applied to the d.c. substrate for PDP.

Examples

Example 1

A photosensitive paste was prepared in the following procedure. First, 4g of γ -methacryloxypropylmethyldimethoxysilane (manufactured by Nippon Unicar Co.) as a first photo-setting component was prepared. In addition, 1g of a mixed solution of an aqueous

0.01N nitric acid solution and ethanol in a molar ratio of 2:1 was prepared. After these components were mixed and sufficiently stirred, the mixture was reacted by allowing to standing at 70°C for 12 hours. Then, the reaction product was dried at 70°C, and water and alcohol were removed by evaporation.

5 To 4g of this dried reaction product, 0.03g of a first photo-setting initiator and 16g of a ceramic powder were added. As the first photo-setting initiator, bis(2,4,6-trimethylbenzoyl)-phenylphosphine oxide commercially available from Ciba Geigy Co. under the trade name of Irgacure 819 was used. This first photo-setting initiator has an absorption edge at a wavelength of about 450 nm. As the ceramic powder, an α -alumina
10 commercially available from Showa Denko Co. under the trade name of Al-45-2 was used. This α -alumina has an average particle diameter of 2.1 μ m.

Then, a mold having a concave portion corresponding to the shape of a rib was prepared. This mold was formed from a second photo-setting component in the presence of 1% by weight of a second photo-setting initiator. As the second photo setting
15 component, an aliphatic urethane acrylate oligomer commercially available from Henschel Co. under the trade name of Photomer 6010 was used. As the second photo-setting initiator, 2-hydroxy-2-methyl-1-phenyl-propan-1-one commercially available from Ciba Geigy Co. under the trade name of Dalocure 1173 was used. This initiator has an absorption edge at a wavelength corresponding to 380 nm. Photopolymerization of the
20 second photo-setting component was conducted by exposure to ultraviolet light of 200 to 450 nm from an ultraviolet light source (trade name: Unicure) manufactured by Ushio Denki Co.

The concave portion of the mold was filled with the above photosensitive paste. Then, a transparent back plate was placed on this mold, thereby making contact with
25 photosensitive paste in the concave portion. Using a fluorescent lamp manufactured by Philips Co., photopolymerization of the first photo-setting component was conducted by exposure to light having a wavelength of 400 to 500 nm for 30 seconds. Exposure to light was conducted simultaneously from both sides of the transparent mold and transparent substrate. Then, a molded article together with the back plate was removed from the mold.
30 In this case, removal of the molded article from the mold could be conducted without

causing breakage of the molded article or back plate. Then, the molded article and back plate were put in a calcinating oven at 500°C to obtain a rib.

Comparative Example 1

5 In this example, the same photosensitive paste and mold as those in Example 1 were used. However, photopolymerization of the first photo-setting component was conducted by using the above ultraviolet light source in place of a fluorescent lamp manufactured by Philips Co. As a result, the back plate could not be removed from the mold, together with
10 back plate, because of strong adhesion between the mold and molded article. The molded article was forcibly removed from the mold, resulting in breakage of the molded article.

Comparative Example 2

In this example, the same photosensitive paste as that in Example 1 was used. However, the mold in this example was made by using the second photo-setting component
15 and first photo-setting initiator of Example 1 in place of the second photo-setting component and second photo-setting initiator. In this case, photopolymerization of the second photo-setting component for obtaining the mold was conducted by using the above ultraviolet light source.

20 After the concave portion of the mold was filled with the above photosensitive paste, photopolymerization of the first photo-setting component for obtaining a rib precursor was conducted by using the above fluorescent lamp. As a result, the back plate could not be removed from the mold, together with back plate, because of strong adhesion between the mold and molded article. The molded article was forcibly removed from the mold, resulting in breakage of the molded article.

Effect of the Invention

25 According to the method of producing the substrate for PDP of the present invention, breakage of the base and rib is avoided and the mold can be repeatedly used.

CLAIMS

What is claimed is:

1. A method of producing a substrate for a plasma display panel by providing a rib on a base, which comprises the steps of:

contacting a rib precursor containing a first photo-setting initiator having a first absorption edge and a first photo-setting component closely with said base;

filling a mold, obtained by photo-setting of a second photo-setting initiator having a second absorption edge whose wavelength is shorter than a wavelength corresponding to said first absorption edge of said first photo-setting initiator, with said rib precursor;

exposing said rib precursor to light having a wavelength longer than a wavelength corresponding to said second absorption edge, thereby setting said rib precursor; and removing said mold.

2. The method according to claim 1, wherein the base and mold are transparent and exposure of the rib precursor to light is conducted via the base and mold.

3. The method according to claim 1 or 2, wherein the mold is flexible.

4. The method according to any one of claims 1 to 3, wherein the first photo-setting initiator has the first absorption edge corresponding to a wavelength of 400 to 500 nm and the second photo-setting initiator has the second absorption edge corresponding to a wavelength of 300 to 400 nm.

5. The method according to any one of claims 1 to 4, wherein the first photo-setting component and second photo-setting component are acrylic resin.

6. The method according to any one of claims 1 to 5, wherein the rib precursor contains a powder of ceramic and optionally contains a powder of glass.

7. A mold for a substrate for a plasma display panel comprising a base and a rib formed from a rib precursor containing a first photo-setting initiator having a first absorption edge and a first photo-setting component, said mold being obtained by photo-setting a second photo-setting component in the presence of a second photo-setting initiator having an absorption edge whose wavelength is shorter than a wavelength corresponding to said first absorption edge of said first photo-setting initiator.
8. The mold according to claim 7, which is flexible.
9. The mold according to claim 7 or 8, which is transparent.

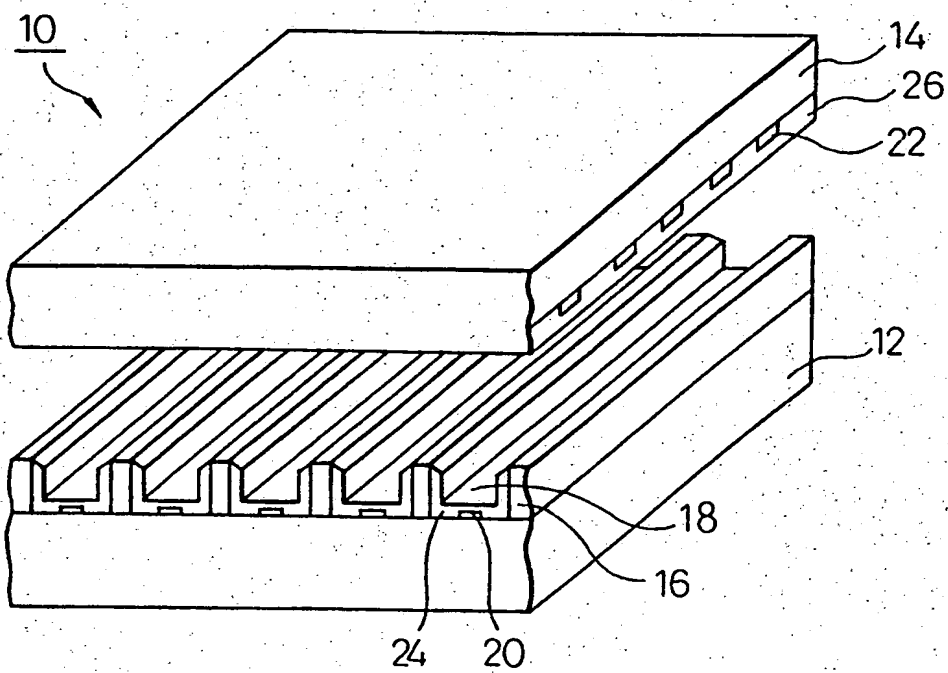
$\frac{1}{2}$ 

Fig. 1

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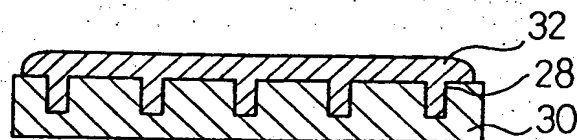


Fig. 2A



Fig. 2B

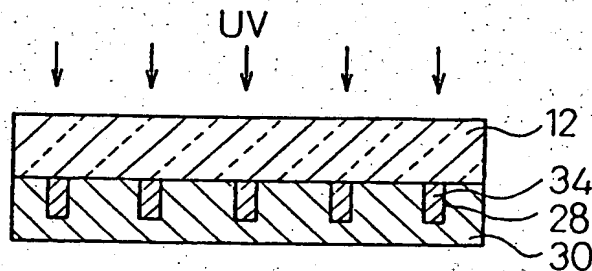


Fig. 2C

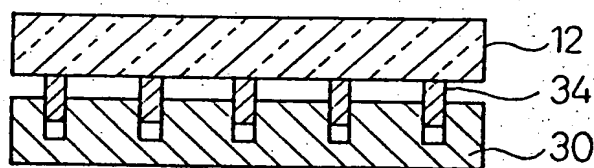


Fig. 2D

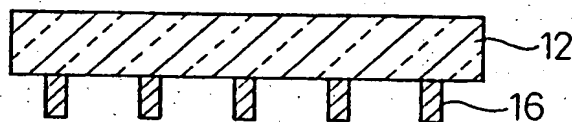


Fig. 2E

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 00/03953

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 H01J9/24 H01J17/16 H01J17/49

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 H01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	FR 2 738 393 A (KYOCERA CORP) 7 March 1997 (1997-03-07) cited in the application page 8, line 11 - line 23 page 20, line 25 - page 22, line 35; figures 8A, 8B	1, 6, 7
A	WO 99 10909 A (MASAKI TAKAKI ; MORIYA GO (JP); ARIZUMI KIWAME (JP); DEGUCHI YUKICH) 4 March 1999 (1999-03-04)	1, 7
P, A	& EP 0 935 275 A (TORAY INDUSTRIES INC) 11 August 1999 (1999-08-11) page 5, line 27 - line 34 page 10, line 20 - line 34 page 12, line 54 - page 22, line 33 --- -/-	1, 7

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"Z" document member of the same patent family

Date of the actual completion of the international search

16 June 2000

Date of mailing of the international search report

26/06/2000

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Schaub, G

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 00/03953

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P, A	WO 99 60446 A (MINNESOTA MINING & MFG) 25 November 1999 (1999-11-25) the whole document	1, 7
A	PATENT ABSTRACTS OF JAPAN vol. 1997, no. 05, 30 May 1997 (1997-05-30) & JP 09 012336 A (ASAHI GLASS CO LTD), 14 January 1997 (1997-01-14) cited in the application abstract	1, 7

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 00/03953

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
FR 2738393	A	07-03-1997	JP 9147754 A	06-06-1997
			JP 9134676 A	20-05-1997
			JP 9259754 A	03-10-1997
			JP 9265905 A	07-10-1997
			JP 10021839 A	23-01-1998
			US 6023130 A	08-02-2000
WO 9910909	A	04-03-1999	JP 11339668 A	10-12-1999
			CN 1237271 T	01-12-1999
			EP 0935275 A	11-08-1999
			JP 11135025 A	21-05-1999
			JP 2000048714 A	18-02-2000
WO 9960446	A	25-11-1999	JP 11344809 A	14-12-1999
			AU 3883399 A	06-12-1999
JP 09012336	A	14-01-1997	NONE	

REPLACED BY
ART 34 AMDT

CLAIMS

What is claimed is:

1. A method of producing a substrate for a plasma display panel by providing a rib on
5 a base, which comprises the steps of:

contacting a rib precursor containing a first photo-setting initiator having a first
absorption edge and a first photo-setting component closely with said base;

filling a mold, obtained by photo-setting of a second photo-setting initiator having a
second absorption edge whose wavelength is shorter than a wavelength corresponding to
10 said first absorption edge of said first photo-setting initiator, with said rib precursor;

exposing said rib precursor to light having a wavelength longer than a wavelength
corresponding to said second absorption edge, thereby setting said rib precursor; and
removing said mold.

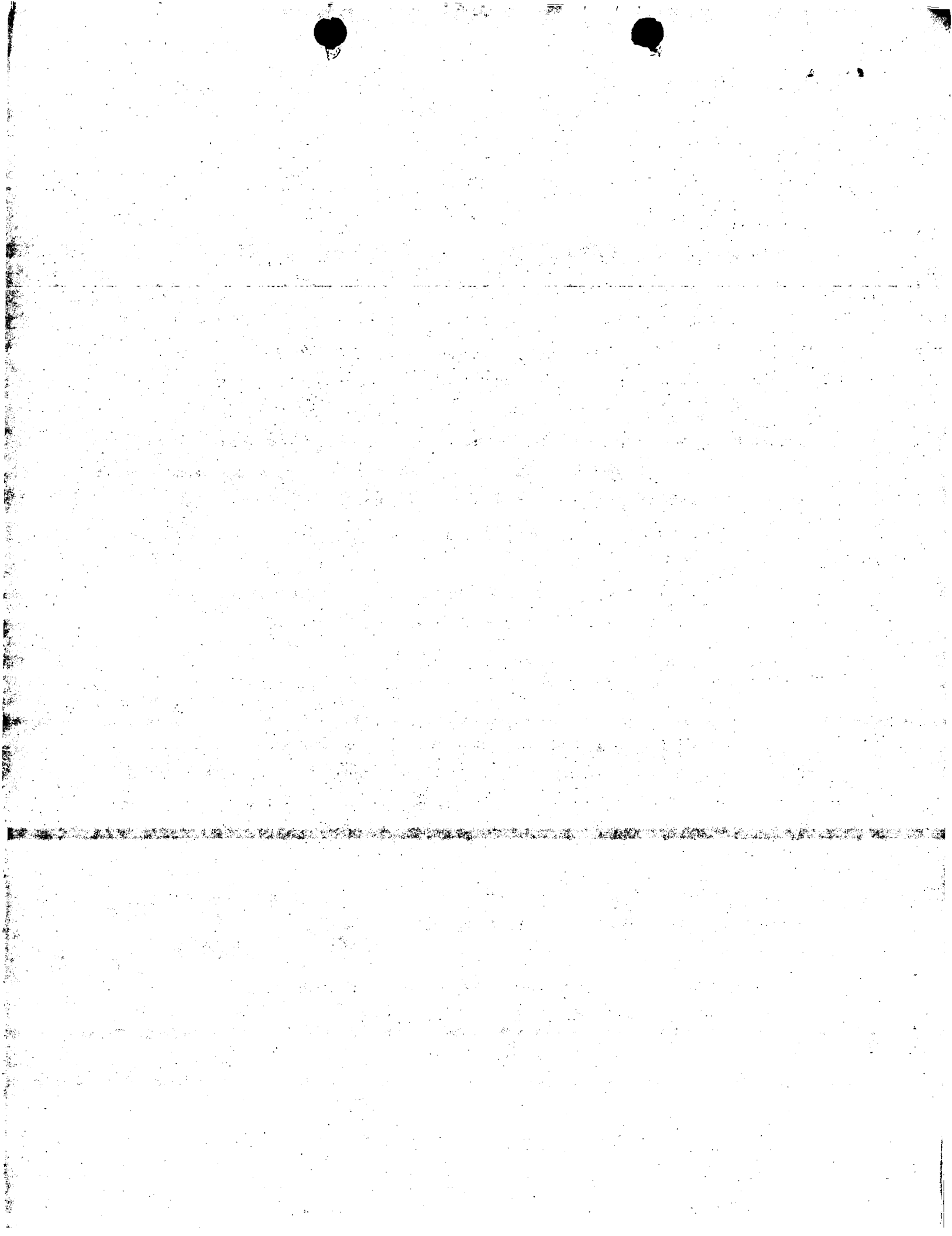
15 2. The method according to claim 1, wherein the base and mold are transparent and
exposure of the rib precursor to light is conducted via the base and mold.

3. The method according to claim 1 or 2, wherein the mold is flexible.

20 4. The method according to any one of claims 1 to 3, wherein the first photo-setting
initiator has the first absorption edge corresponding to a wavelength of 400 to 500 nm and
the second photo-setting initiator has the second absorption edge corresponding to a
wavelength of 300 to 400 nm.

25 5. The method according to any one of claims 1 to 4, wherein the first photo-setting
component and second photo-setting component are acrylic resin.

6. The method according to any one of claims 1 to 5, wherein the rib precursor
contains a powder of ceramic and optionally contains a powder of glass.



7. A mold for a substrate for a plasma display panel comprising a base and a rib formed from a rib precursor containing a first photo-setting initiator having a first absorption edge and a first photo-setting component, said mold being obtained by photo-setting a second photo-setting component in the presence of a second photo-setting initiator having an absorption edge whose wavelength is shorter than a wavelength corresponding to said first absorption edge of said first photo-setting initiator.

8. The mold according to claim 7, which is flexible.

9. The mold according to claim 7 or 8, which is transparent.

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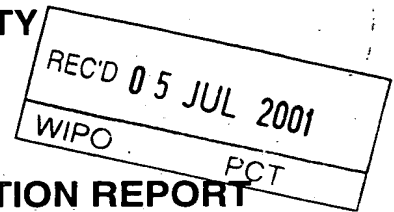
1000000

PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)



Applicant's or agent's file reference Hi-bu 001969wo	FOR FURTHER ACTION See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)	
International application No. PCT/US00/03953	International filing date (day/month/year) 16/02/2000	Priority date (day/month/year) 25/03/1999
International Patent Classification (IPC) or national classification and IPC H01J9/24		
Applicant MINNESOTA MINING AND MANUFACTURING COMPANY et al.		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.


2. This REPORT consists of a total of 7 sheets, including this cover sheet.

- ☒ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

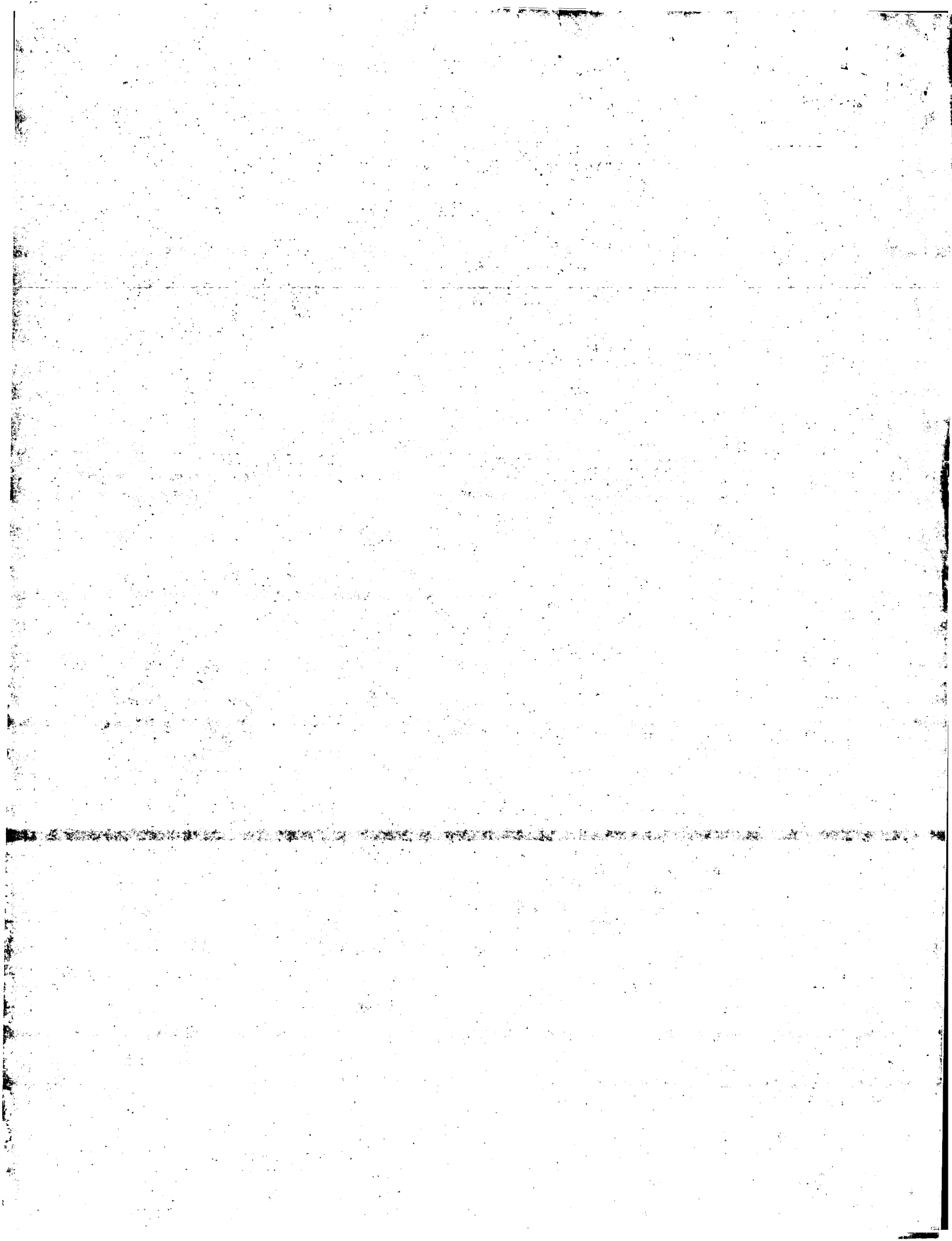
These annexes consist of a total of 3 sheets.

3. This report contains indications relating to the following items:

- I ☒ Basis of the report
- II ☐ Priority
- III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- IV ☐ Lack of unity of invention
- V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI ☒ Certain documents cited
- VII ☒ Certain defects in the international application
- VIII ☒ Certain observations on the international application

Date of submission of the demand 16/08/2000	Date of completion of this report 03.07.2001
Name and mailing address of the international preliminary examining authority:  European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized officer Meul, H Telephone No. +49 89 2399 2494





INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/US00/03953

I. Basis of the report

1. With regard to the **elements** of the international application (*Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17)*):
Description, pages:

1-10 as originally filed

Claims, No.:

1-11 as received on 03/04/2001 with letter of 02/04/2001

Drawings, sheets:

1/2,2/2 as originally filed

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
- ☐ the language of publication of the international application (under Rule 48.3(b)).
- ☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- ☐ contained in the international application in written form.
- ☐ filed together with the international application in computer readable form.
- ☐ furnished subsequently to this Authority in written form.
- ☐ furnished subsequently to this Authority in computer readable form.
- ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

- ☐ the description, pages:
- ☐ the claims, Nos.:

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

International application No. PCT/US00/03953

☐ the drawings, sheets:

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)

6. Additional observations, if necessary:

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims	1-11
	No:	Claims	
Inventive step (IS)	Yes:	Claims	1-11
	No:	Claims	
Industrial applicability (IA)	Yes:	Claims	1-11
	No:	Claims	

2. Citations and explanations
see separate sheet

VI. Certain documents cited

1. Certain published documents (Rule 70.10)

and / or

2. Non-written disclosures (Rule 70.9)

see separate sheet

VII. Certain defects in the international application

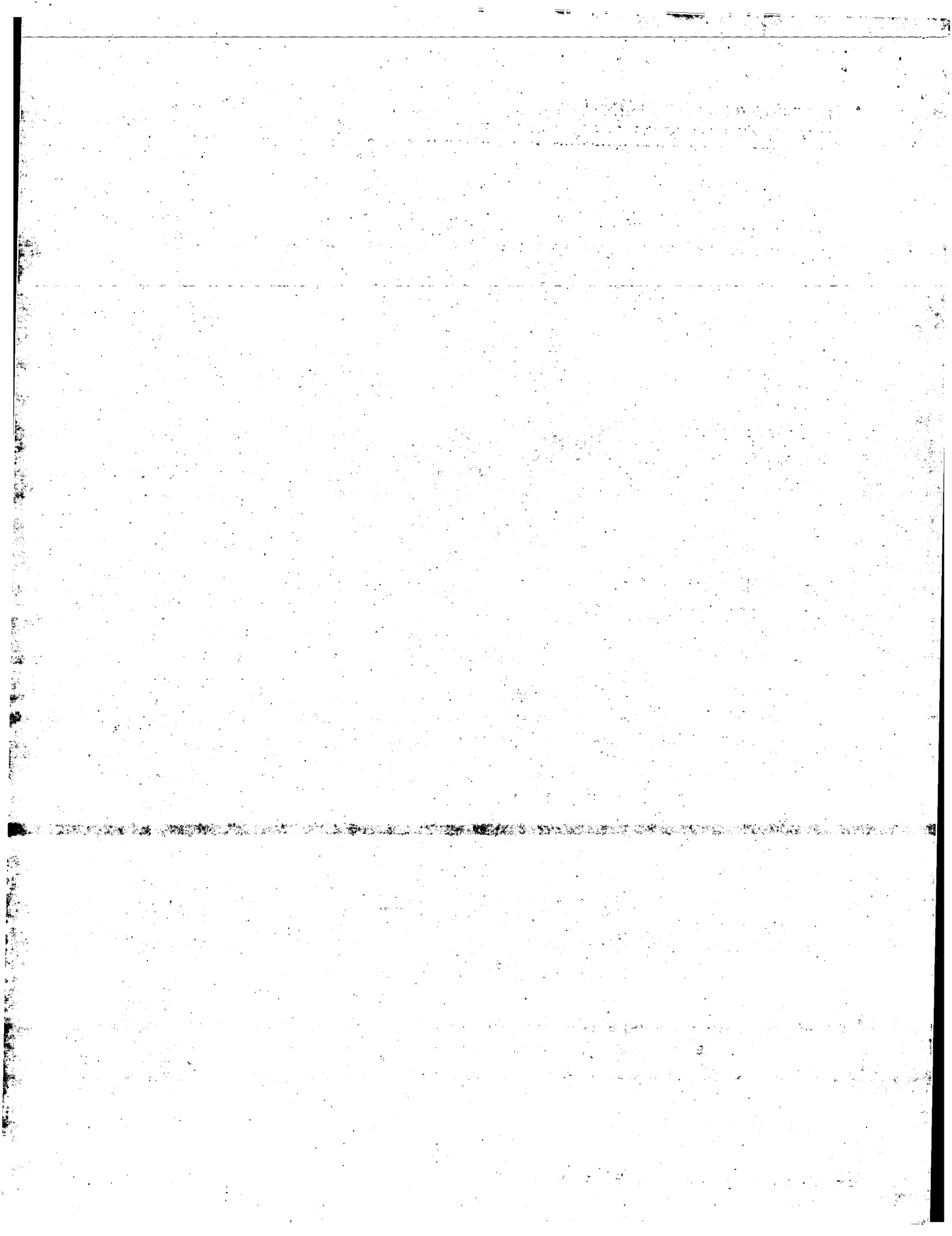
The following defects in the form or contents of the international application have been noted:
see separate sheet

VIII. Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:
see separate sheet

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

International application No. PCT/US00/03953



Re Item V

Reasoned statement under Article 35 (2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

Technical field

The invention relates to a method of producing a substrate for a plasma display panel by providing a rib on a base and to an assembly of a mould and a rib precursor used in the method.

Closest prior art

WO 99/10909 A and corresponding EP 0 935 275 A1 (=D1) disclose a process for fabricating a plasma display panel comprising a base and a rib wherein a mould formed of silicone is filled with a barrier rib paste and contacted with a base. Subsequently, the mould is removed and the rib precursor is fired.

Problem

To provide a process and a mould for mass production of a substrate for a plasma display panel, capable of being repeatedly used without causing breakage of the base or the ribs (see p. 1, l. 21 to p. 2, l. 9 of the present description).

Solution

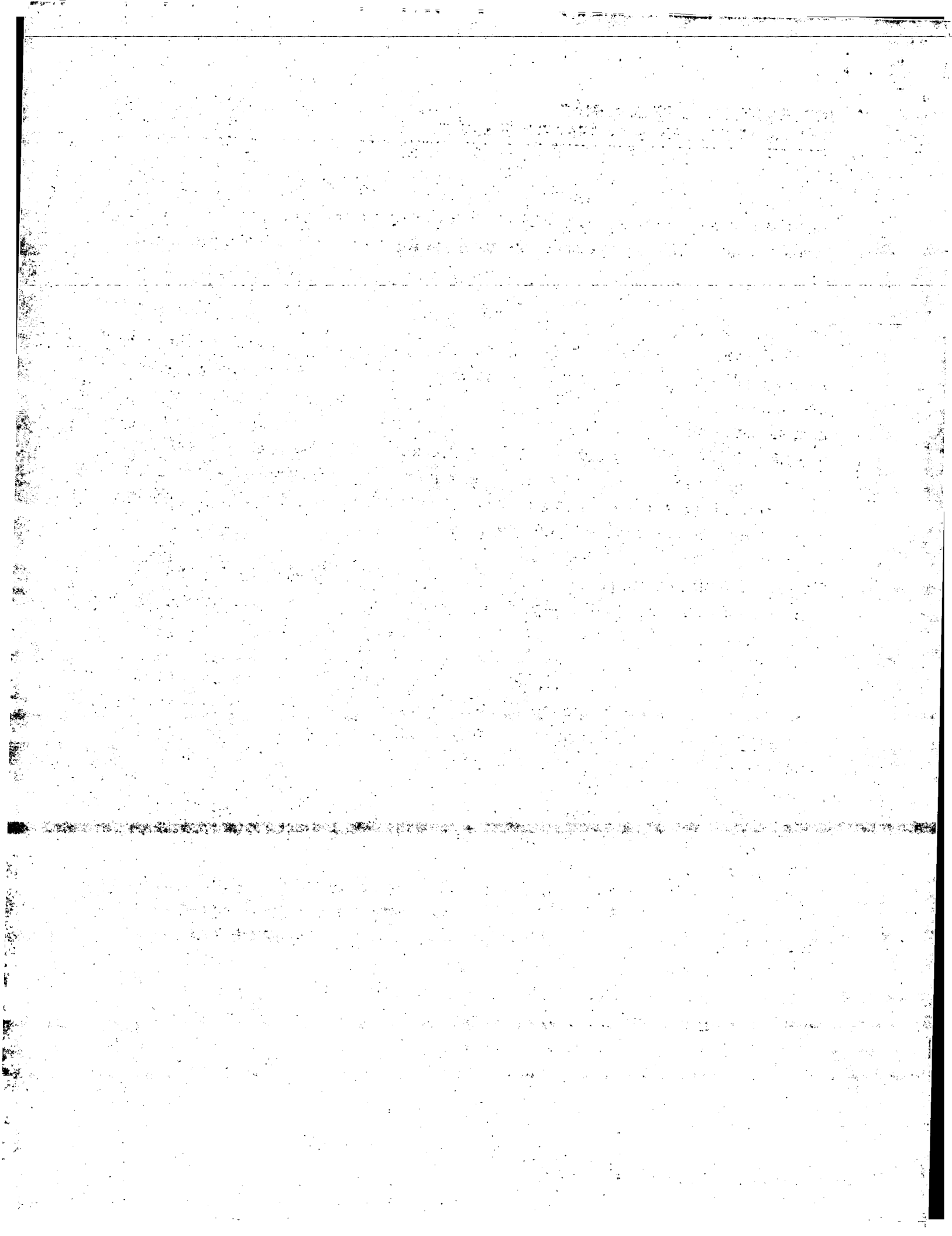
A rib precursor containing a first photo-setting initiator having a first absorption edge and a first photo-setting component is filled into a mould obtained by photo-setting of a second photo-setting initiator having a second absorption edge whose wavelength is shorter than a wavelength corresponding to said first absorption edge of said first photo-setting initiator and said rib precursor is exposed to light having a wavelength longer than a wavelength corresponding to said second absorption edge (see claims 1 and 2 for the method and claim 8 for the assembly of a mould and a rib precursor).

Assessment

None of the presently available prior art documents discloses or fairly suggests the present combination of mould and rib precursor materials. More specifically, the documents WO 99/10909 A (=D1), FR 2738393 A, and JP 09-012336 A do not teach to use a photo-setting component in the mould and/or the rib material.

The non-prepublished document WO 99/60446 A (see section VI of the present report) discloses a method of producing a substrate for a plasma display panel using a photosensitive rib paste and a plastic mould.

EP 0196033 A describes the photofabrication of master relief patterns by using a



**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT - SEPARATE SHEET**

International application No. PCT/US00/03953

material comprising a photo-setting component and a photo-setting initiator. There is no incitement to fill the master relief with another photosensitive material having an absorption edge whose wavelength is longer than a wavelength corresponding to an absorption edge of the master relief pattern and to use this assembly for fabricating a substrate for a plasma display panel.

Therefore, the subject-matter of independent claims 1, 2 and 8 is novel and involves an inventive step. Dependent claims 3-7 and 9-11 define advantageous developments of the methods of claims 1 and 2 and the assembly of claim 8, respectively, and as such also meet the requirements of the PCT with respect to novelty and inventive step.

Re Item VI

Certain documents cited

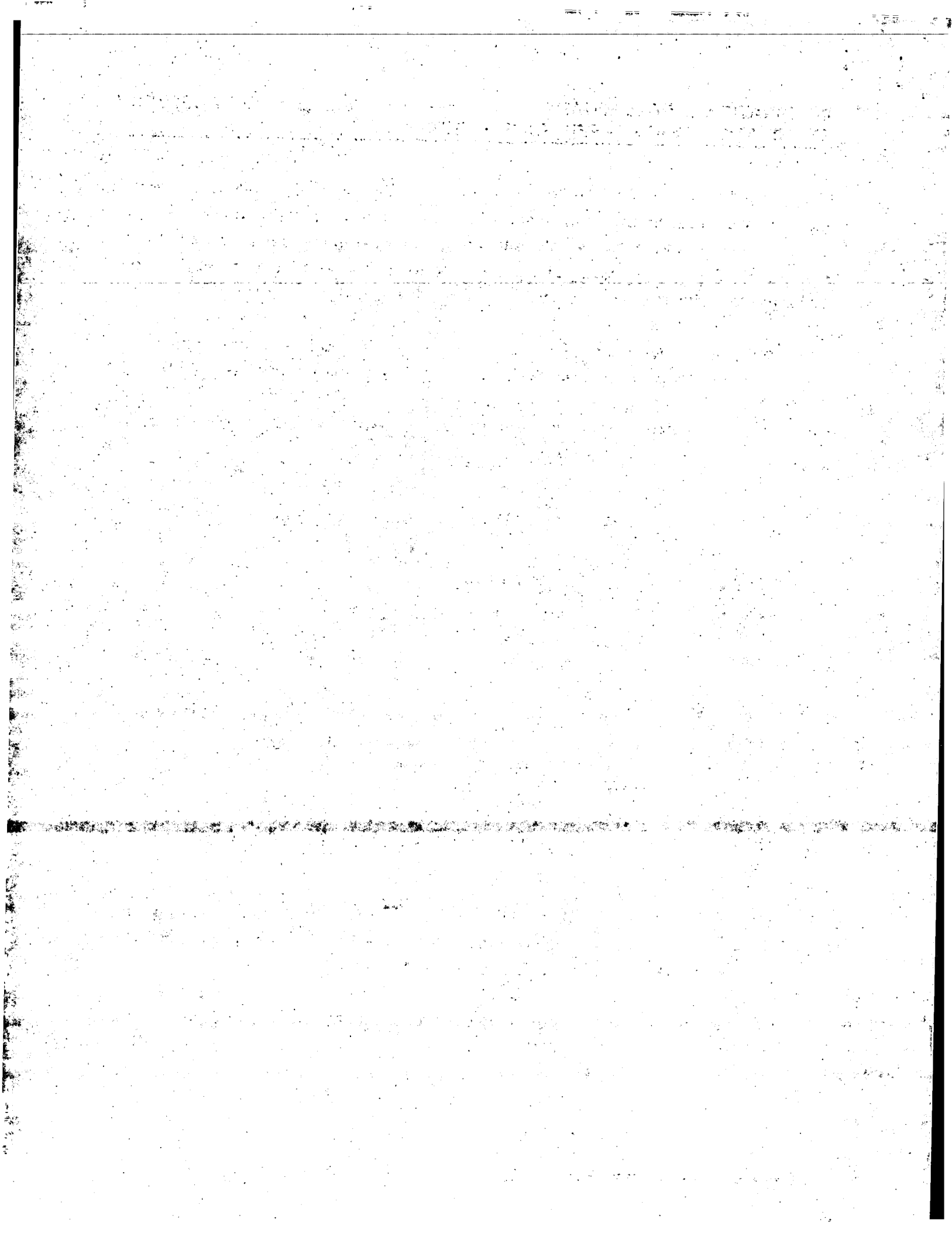
Certain published documents (Rule 70.10)

Application No Patent No	Publication date (day/month/year)	Filing date (day/month/year)	Priority date (valid claim) (day/month/year)
WO 99/60446 A1	25.11.99	05.05.99	18.05.98

Re Item VII

Certain defects in the international application

1. The unit 'cps' employed on page 6 is not additionally expressed in terms of the unit stipulated by Rule 10.1 PCT.
2. Contrary to the requirements of Rule 5.1 (a) (ii) PCT, the relevant background art disclosed in the documents D1 and D2 is not mentioned in the description, nor are these documents identified therein.
3. The description is not in conformity with the claims as required by Rule 5.1 (a) (iii) PCT.



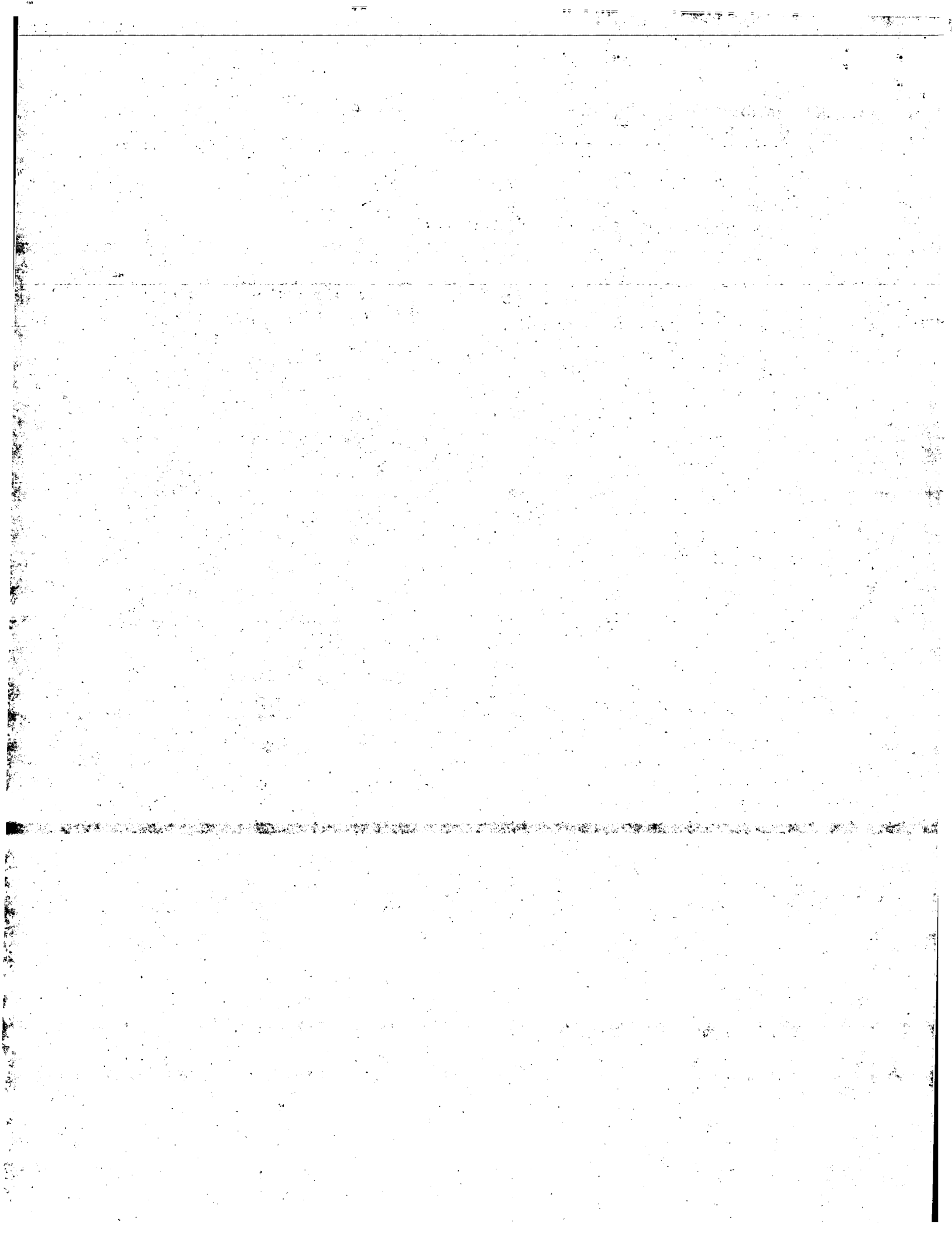
**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT - SEPARATE SHEET**

International application No. PCT/US00/03953

Re Item VIII

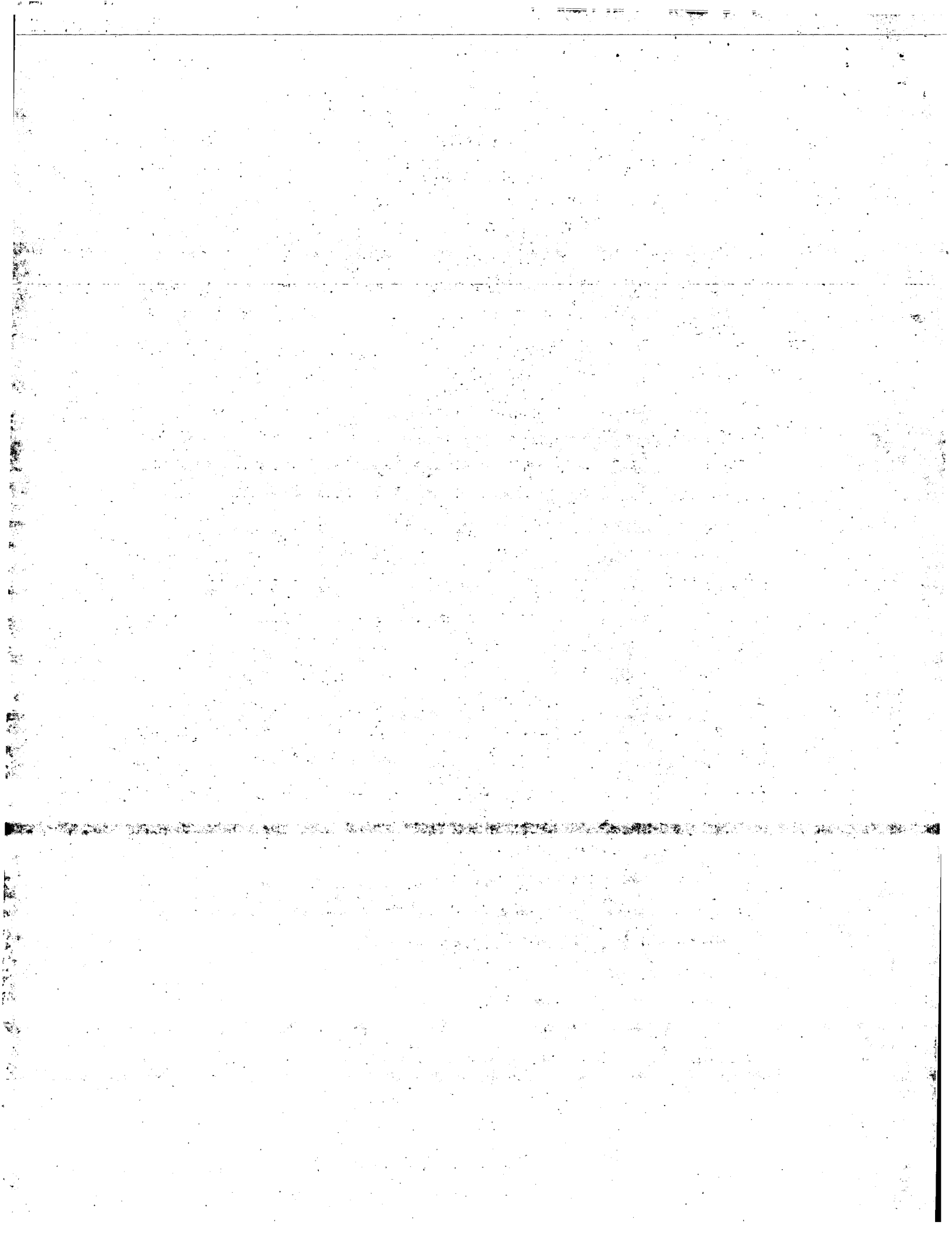
Certain observations on the international application

1. A lack of clarity arises in claim 2 because there is no antecedent for 'said first absorption edge of said first photo-setting initiator' in the preceding part of the claim.



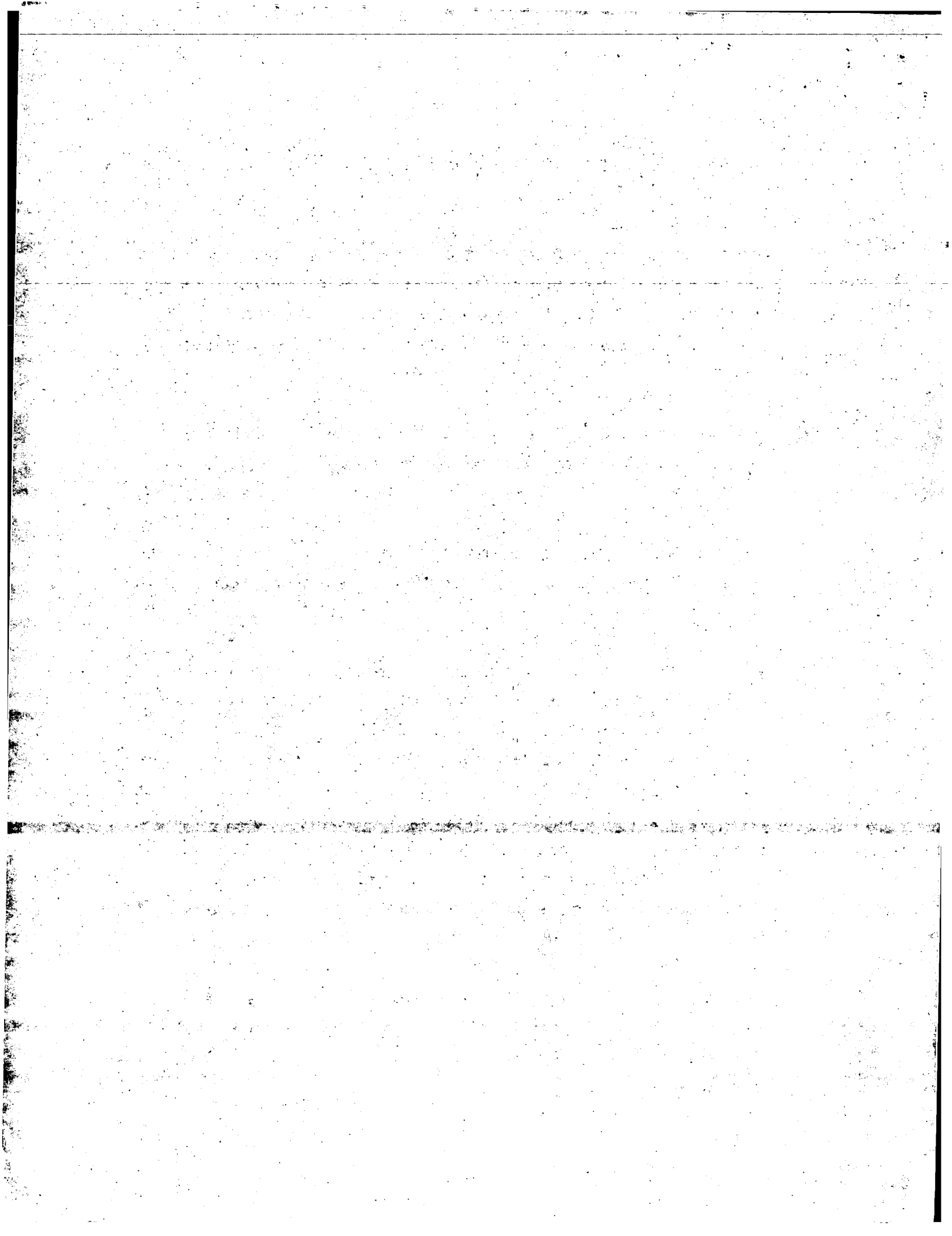
CLAIMS

1. A method of producing a substrate for a plasma display panel by providing a rib on a base, which comprises the steps of
 - contacting a rib precursor containing a first photo-setting initiator having a first absorption edge and a first photo-setting component closely with said base,
 - filling a mold, obtained by photo-setting of a second photo-setting initiator having a second absorption edge whose wavelength is shorter than a wavelength corresponding to said first absorption edge of said first photo-setting initiator, with said rib precursor,
 - exposing said rib precursor to light having a wavelength longer than a wavelength corresponding to said second absorption edge, thereby setting said rib precursor, and
 - removing said mold.
2. A method of producing a substrate for a plasma display panel by providing a rib on a base, which comprises the steps of
 - filling a mold, obtained by photo-setting of a second photo-setting initiator having a second absorption edge whose wavelength is shorter than a wavelength corresponding to said first absorption edge of said first photo-setting initiator, with a rib precursor containing a first photo-setting initiator having a first absorption edge and a first photo-setting component,
 - contacting said rib precursor closely with said base,
 - exposing said rib precursor to light having a wavelength longer than a wavelength corresponding to said second absorption edge, thereby setting said rib precursor, and
 - removing said mold.
3. The method according to claim 1 or 2, wherein the base and mold are transparent and exposure of the rib precursor to light is conducted via the base and mold.



- 2 -

4. The method according any one of claims 1 to 3, wherein the mold is flexible.
5. The method according to any one of claims 1 to 4, wherein the first photo-setting initiator has the first absorption edge corresponding to a wavelength of 400 to 500 nm and the second photo-setting initiator has the second absorption edge corresponding to a wavelength of 300 to 400 nm.
6. The method according to any one of claims 1 to 5, wherein the first photo-setting component and second photo-setting component are acrylic resin.
7. The method according to any one of claims 1 to 6, wherein the rib precursor contains a powder of ceramic and optionally contains a powder of glass.
8. An assembly of a mold for making a substrate for a plasma display device panel comprising a base and ribs, said mold having concave portions, and a rib precursor for forming said ribs said rib precursor being disposed in said concave portions of said mold and containing a first photo-setting initiator having a first absorption edge and a first photo-setting component, said mold being obtained by photo-setting a second photo-setting component in the presence of a second photo-setting initiator having an absorption edge whose wavelength is shorter than a wavelength corresponding to said ~~first~~ absorption edge of said first photo-setting initiator.
9. The assembly according to claim 8, wherein said mold is flexible.
10. The assembly according to claim 8 or 9, wherein said mold is transparent.



- 3 -

11. The assembly according to any one of claims 7 to 9, further comprising a glass substrate forming the base of the substrate for the plasma display panel, said glass substrate contacting said rib precursor disposed in the concave portions of said mold.

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DEC 17 2001
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INTERNATIONAL COOPERATION TREATY

PCT

INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference 54769PCT1A	FOR FURTHER ACTION see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.	
International application No. PCT/US 00/ 03953	International filing date (day/month/year) 16/02/2000	(Earliest) Priority Date (day/month/year) 25/03/1999
Applicant MINNESOTA MINING AND MANUFACTURING COMPANY et al.		

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 3 sheets.

☒ It is also accompanied by a copy of each prior art document cited in this report.

1. Basis of the report

a. With regard to the **language**, the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.

☐ the international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).

b. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international search was carried out on the basis of the sequence listing:

☐ contained in the international application in written form.

☐ filed together with the international application in computer readable form.

☐ furnished subsequently to this Authority in written form.

☐ furnished subsequently to this Authority in computer readable form.

☐ the statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.

☐ the statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished

2. ☐ **Certain claims were found unsearchable** (See Box I).

3. ☐ **Unity of invention is lacking** (see Box II).

4. With regard to the **title**,

☒ the text is approved as submitted by the applicant.

☐ the text has been established by this Authority to read as follows:

5. With regard to the **abstract**,

☒ the text is approved as submitted by the applicant.

☐ the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

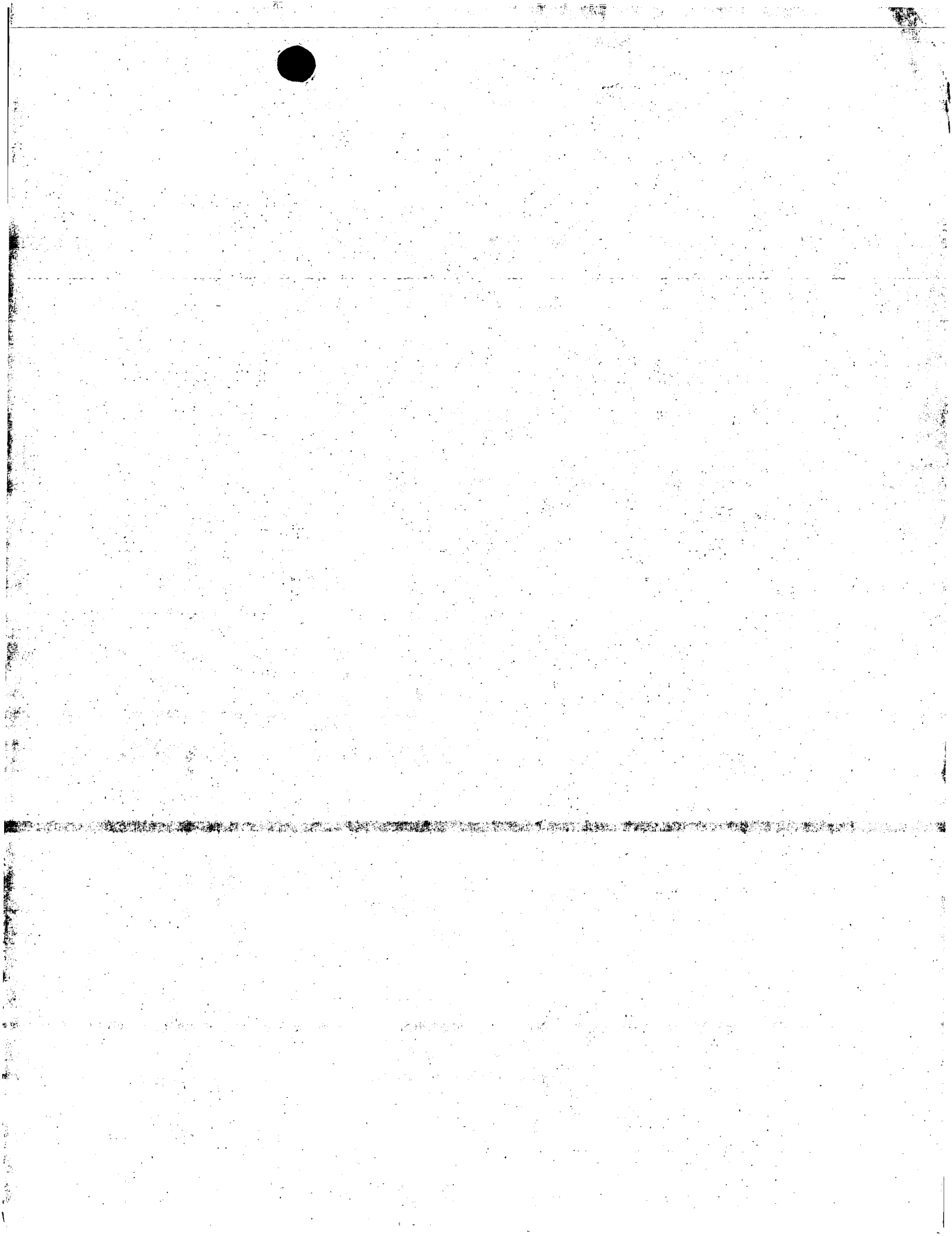
6. The figure of the **drawings** to be published with the abstract is Figure No.

☒ as suggested by the applicant.

☐ because the applicant failed to suggest a figure.

☐ because this figure better characterizes the invention.

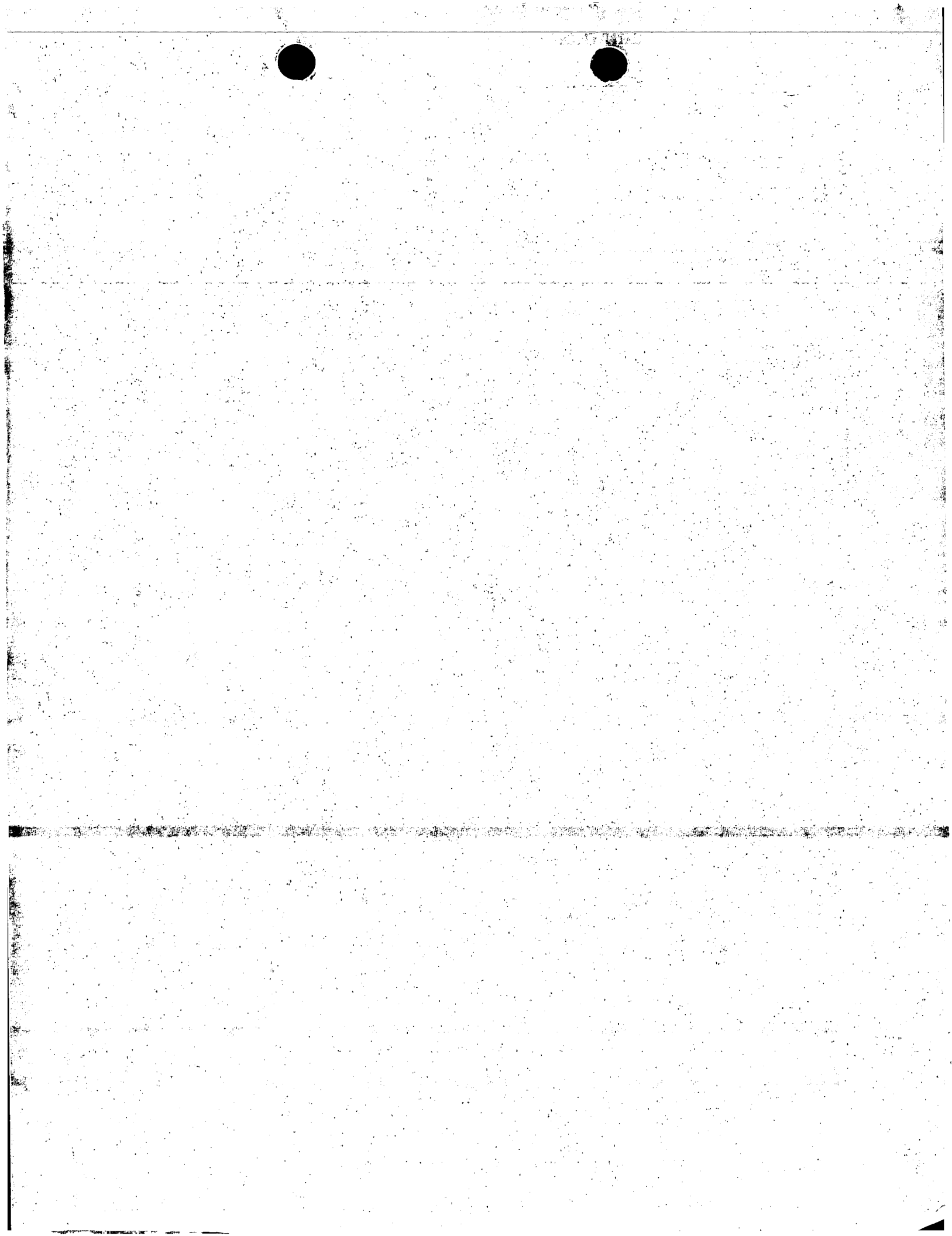
1
☐ None of the figures.



INTERNATIONAL SEARCH REPORT

International Application No.
US 00/03953

A. CLASSIFICATION OF SUBJECT MATTER		
IPC 7 H01J9/24 H01J17/16 H01J17/49		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols) IPC 7 H01J		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practical, search terms used)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	FR 2 738 393 A (KYOCERA CORP) 7 March 1997 (1997-03-07) cited in the application page 8, line 11 - line 23 page 20, line 25 - page 22, line 35; figures 8A, 8B	1, 6, 7
A	WO 99 10909 A (MASAKI TAKAKI ; MORIYA GO (JP); ARIZUMI KIWAME (JP); DEGUCHI YUKICH) 4 March 1999 (1999-03-04)	1, 7
P, A	& EP 0 935 275 A (TORAY INDUSTRIES INC) 11 August 1999 (1999-08-11) page 5, line 27 - line 34 page 10, line 20 - line 34 page 12, line 54 - page 22, line 33	1, 7
-/--		
<input checked="" type="checkbox"/> Further documents are listed in the continuation of box C. <input checked="" type="checkbox"/> Patent family members are listed in annex.		
* Special categories of cited documents : "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. "&" document member of the same patent family		
Date of the actual completion of the international search		Date of mailing of the international search report
16 June 2000		26/06/2000
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016		Authorized officer Schaub, G

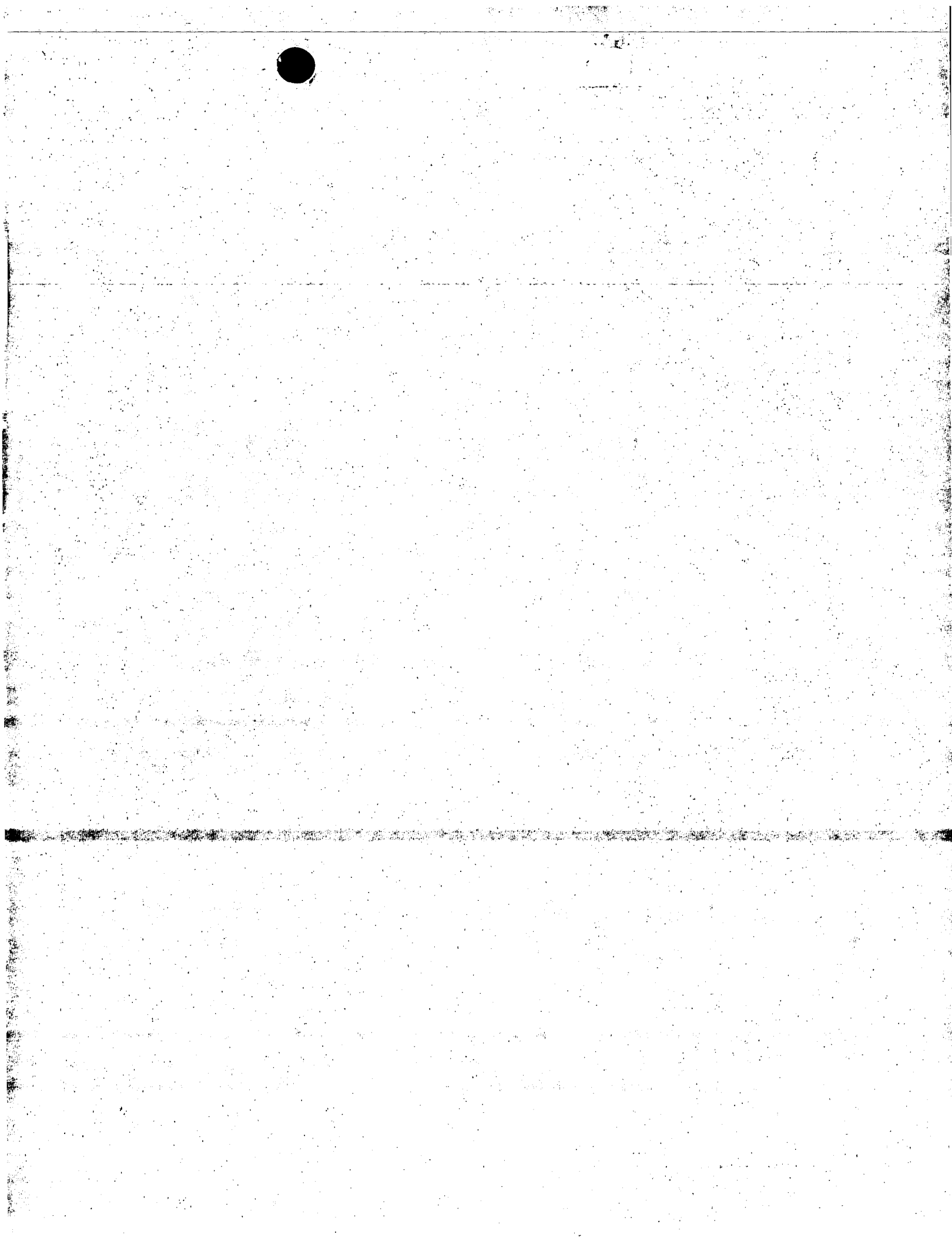


INTERNATIONAL SEARCH REPORT

International Application No

US 00/03953

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P, A	WO 99 60446 A (MINNESOTA MINING & MFG) 25 November 1999 (1999-11-25) the whole document ---	1,7
A	PATENT ABSTRACTS OF JAPAN vol. 1997, no. 05, 30 May 1997 (1997-05-30) & JP 09 012336 A (ASAHI GLASS CO LTD), 14 January 1997 (1997-01-14) cited in the application abstract -----	1,7



INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

US 00/03953

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
FR 2738393	A	07-03-1997	JP 9147754 A	06-06-1997
			JP 9134676 A	20-05-1997
			JP 9259754 A	03-10-1997
			JP 9265905 A	07-10-1997
			JP 10021839 A	23-01-1998
			US 6023130 A	08-02-2000
WO 9910909	A	04-03-1999	JP 11339668 A	10-12-1999
			CN 1237271 T	01-12-1999
			EP 0935275 A	11-08-1999
			JP 11135025 A	21-05-1999
			JP 2000048714 A	18-02-2000
WO 9960446	A	25-11-1999	JP 11344809 A	14-12-1999
			AU 3883399 A	06-12-1999
JP 09012336	A	14-01-1997	NONE	

EUROPEAN PATENT OFFICE

Pat nt Abstracts of Japan

PUBLICATION NUMBER : 09012336
PUBLICATION DATE : 14-01-97

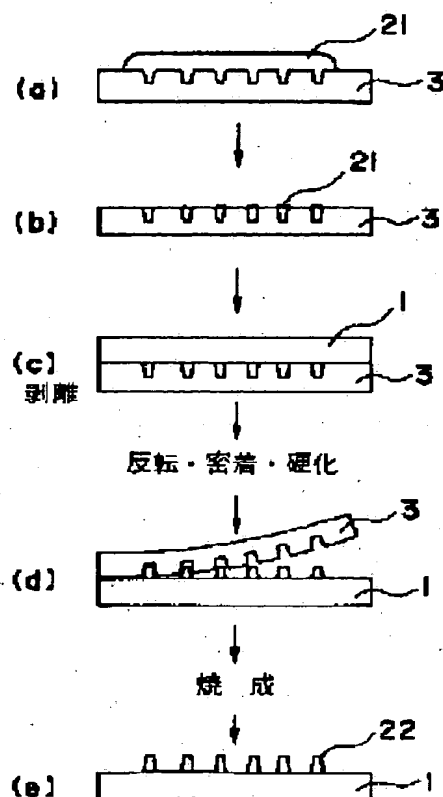
APPLICATION DATE : 26-06-95
APPLICATION NUMBER : 07159263

APPLICANT : ASAHI GLASS CO LTD;

INVENTOR : ISEDA TORU;

INT.CL. : C03C 17/04 B05D 5/06 B05D 7/00
H01J 9/02 H01J 9/24

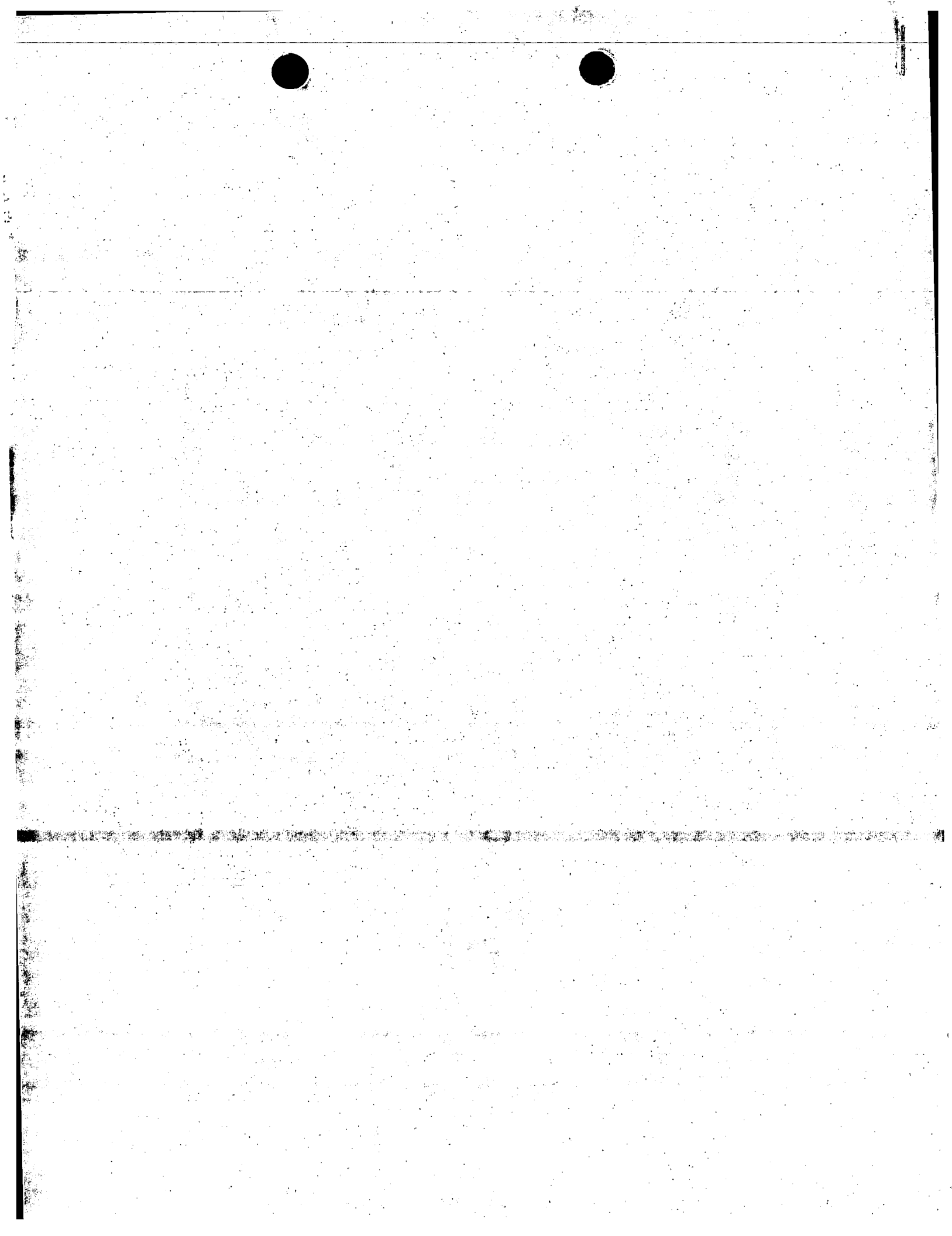
TITLE : FORMATION OF PARTITION WALL
ONTO SUBSTRATE



ABSTRACT : PURPOSE: To make it possible to form a thick coating layer with one time of stage and to form finer partitions by molding a coating liquid contg. a material forming partitions with a molding material and parting the moldings from molds after curing at the time of forming the partitions on a substrate surface.

CONSTITUTION: The coating liquid 21 consisting essentially of fine powder of low melting glass contg. an adhesive is applied on the mold material 3 and a coating liquid layer is formed on the mold material 3. The excess coating liquid 21 built up on the surface of the mold material 3 is then scraped off by a scraper to flatten the surface of the mold material 3. Next, the glass substrate 1 is placed on the mold material 3 and the entire part is inverted to bring the side formed with the recessed parts of the mold material 3 into tight contact with the glass substrate 1. After the coating liquid 21 is cured, the mold material 3 is peeled from the glass substrate 1. Finally, the partitions 22 consisting of the cured coating liquid is calcined to form the glassy partitions. The partitions suitable for a plasma display device or a liquid crystal display device executing scanning by a plasma discharge are formed.

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PATENT COOPERATION TREATY

PCT

INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference 54769PCT1A	FOR FURTHER ACTION		see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.
International application No. PCT/US 00/ 03953	International filing date (day/month/year) 16/02/2000	(Earliest) Priority Date (day/month/year) 25/03/1999	
Applicant MINNESOTA MINING AND MANUFACTURING COMPANY et al.			

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 3 sheets.

☒ It is also accompanied by a copy of each prior art document cited in this report.

1. Basis of the report

a. With regard to the **language**, the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item:

☐ the international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).

b. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international search was carried out on the basis of the sequence listing:

☐ contained in the international application in written form.

☐ filed together with the international application in computer readable form.

☐ furnished subsequently to this Authority in written form.

☐ furnished subsequently to this Authority in computer readable form.

☐ the statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.

☐ the statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished

2. ☐ **Certain claims were found unsearchable** (See Box I).

3. ☐ **Unity of invention is lacking** (see Box II).

4. With regard to the **title**,

☒ the text is approved as submitted by the applicant.

☐ the text has been established by this Authority to read as follows:

5. With regard to the **abstract**,

☒ the text is approved as submitted by the applicant.

☐ the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. The figure of the **drawings** to be published with the abstract is Figure No.

☒ as suggested by the applicant.

☐ because the applicant failed to suggest a figure.

☐ because this figure better characterizes the invention.

1 _____
☐ None of the figures.

INTERNATIONAL SEARCH REPORT

International Application No

US 00/03953

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 H01J9/24 H01J17/16 H01J17/49

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 H01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	FR 2 738 393 A (KYOCERA CORP) 7 March 1997 (1997-03-07) cited in the application page 8, line 11 - line 23 page 20, line 25 - page 22, line 35; figures 8A, 8B	1, 6, 7
A	WO 99 10909 A (MASAKI TAKAKI ; MORIYA GO (JP); ARIZUMI KIWAME (JP); DEGUCHI YUKICH) 4 March 1999 (1999-03-04)	1, 7
P, A	& EP 0 935 275 A (TORAY INDUSTRIES INC) 11 August 1999 (1999-08-11) page 5, line 27 - line 34 page 10, line 20 - line 34 page 12, line 54 - page 22, line 33	1, 7
	--- -/--	



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

16 June 2000

Date of mailing of the international search report

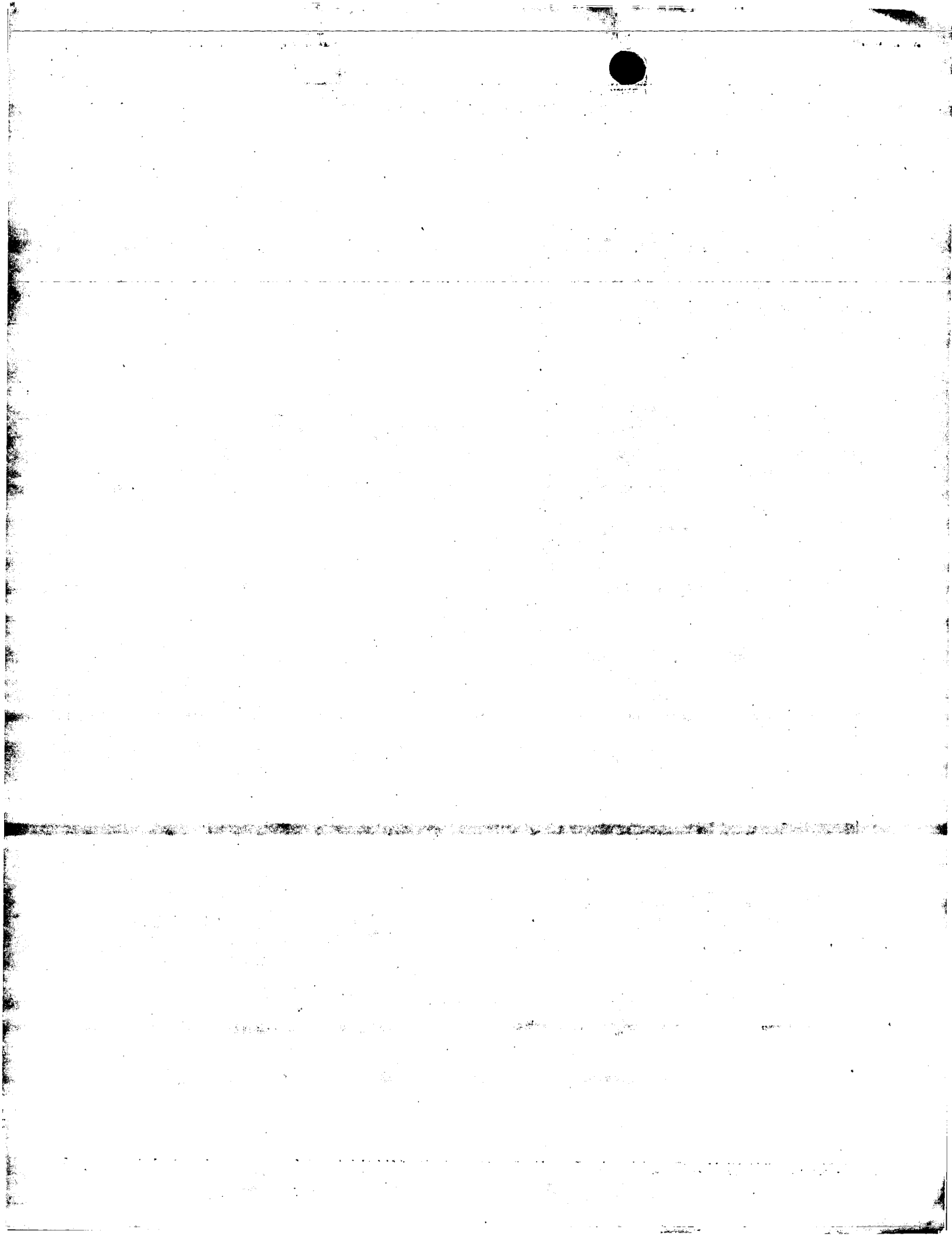
26/06/2000

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Schaub, G



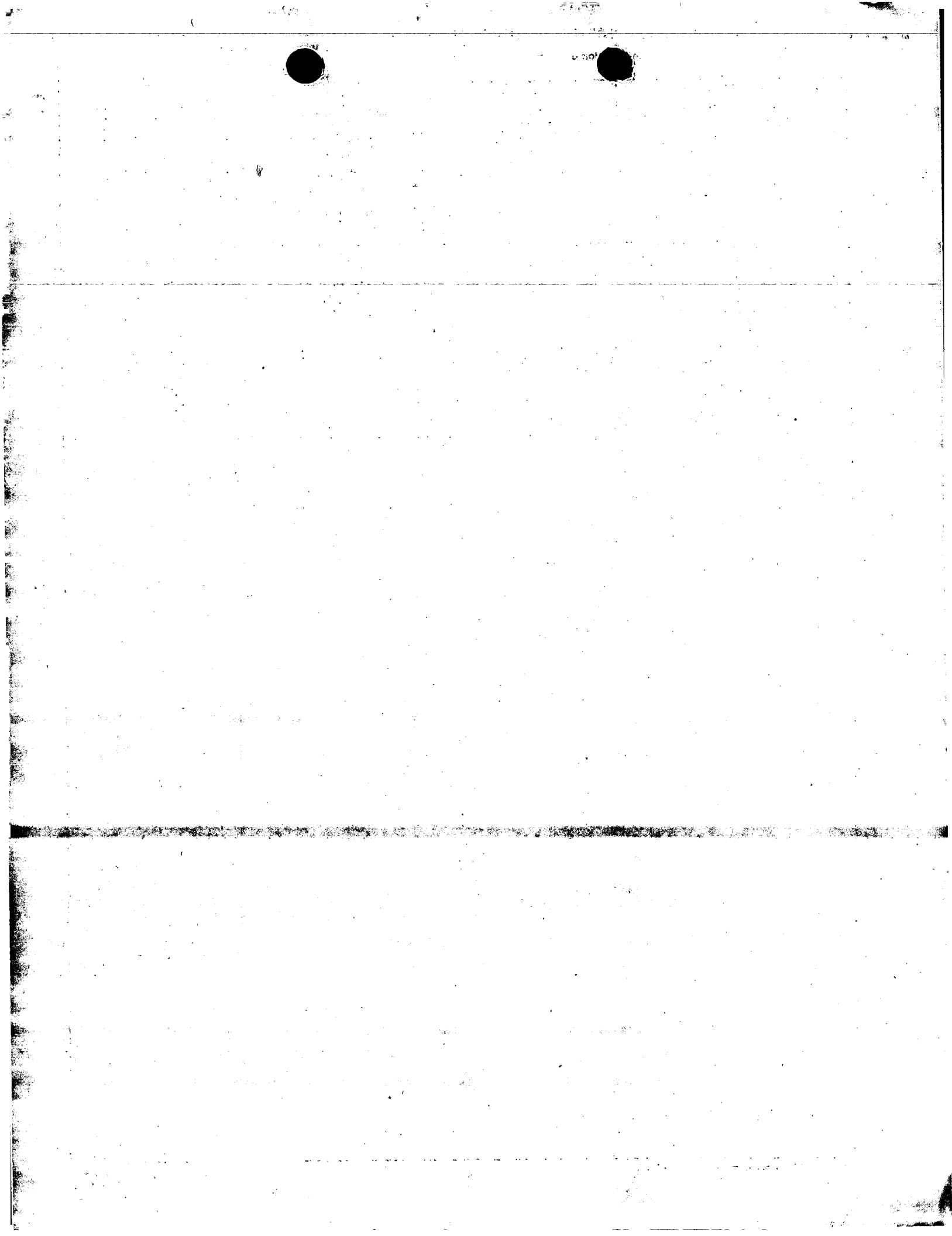
INTERNATIONAL SEARCH REPORT

International Application No.

/US 00/03953

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P, A	WO 99 60446 A (MINNESOTA MINING & MFG) 25 November 1999 (1999-11-25) the whole document -----	1, 7
A	PATENT ABSTRACTS OF JAPAN vol. 1997, no. 05, 30 May 1997 (1997-05-30) & JP 09 012336 A (ASAHI GLASS CO LTD), 14 January 1997 (1997-01-14) cited in the application abstract -----	1, 7



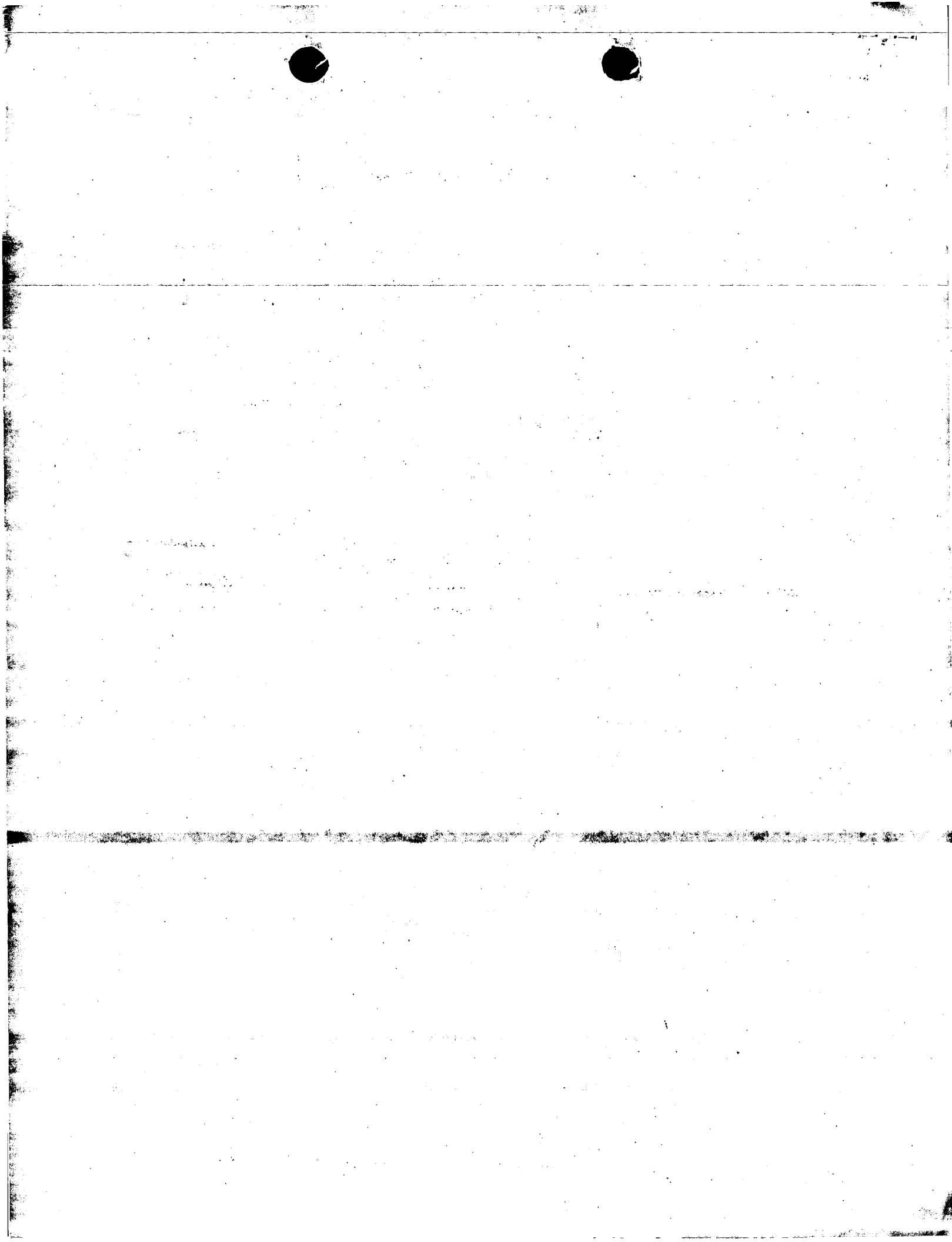
INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

/US 00/03953

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
FR 2738393	A	07-03-1997	JP 9147754 A	06-06-1997
			JP 9134676 A	20-05-1997
			JP 9259754 A	03-10-1997
			JP 9265905 A	07-10-1997
			JP 10021839 A	23-01-1998
			US 6023130 A	08-02-2000
WO 9910909	A	04-03-1999	JP 11339668 A	10-12-1999
			CN 1237271 T	01-12-1999
			EP 0935275 A	11-08-1999
			JP 11135025 A	21-05-1999
			JP 2000048714 A	18-02-2000
WO 9960446	A	25-11-1999	JP 11344809 A	14-12-1999
			AU 3883399 A	06-12-1999
JP 09012336	A	14-01-1997	NONE	



PATENT COOPERATION TREATY

From the RECEIVING OFFICE

PCT

To:

ROBERT J. PECHMAN
OFFICE OF INTELLECTUAL PROPERTY COUNSEL
POST OFFICE BOX 33427
SAINT PAUL, MN 55133-3427

OFFICE OF INTELLECTUAL
PROPERTY COUNSEL
3M INNOVATIVE PROPERTIES COMPANY

NOTIFICATION OF THE INTERNATIONAL
APPLICATION NUMBER AND OF THE
INTERNATIONAL FILING DATE

(PCT Rule 20.5(c))

MAR 20 2000

Date of mailing
(day/month/year)

16 MAR 2000

Applicant's or agent's file reference
54769PCT1A, 003

REFERRED TO

IMPORTANT NOTIFICATION

International application No.

PCT/US00/03953

International filing date (day/month/year)

16 FEB 00

Priority date (day/month/year)

25 MAR 99

Applicant

MINNESOTA MINING AND MANUFACTURING COMPANY

Title of the invention

METHOD OF PRODUCING SUBSTRATE FOR PLASMA DISPLAY
PANEL AND MOLD USED IN THE METHOD

1. The applicant is hereby notified that the international application has been accorded the international application number and the international filing date indicated above.

2. The applicant is further notified that the record copy of the international application:



was transmitted to the International Bureau on

16 MAR 2000



has not yet been transmitted to the International Bureau for the reason indicated below and a copy of this notification has been sent to the International Bureau*:



because the necessary national security clearance has not yet been obtained.



because (reason to be specified):

* The International Bureau monitors the transmittal of the record copy by the receiving Office and will notify the applicant (with Form PCT/IB/301) of its receipt. Should the record copy not have been received by the expiration of 14 months from the priority date, the International Bureau will notify the applicant (Rule 22.1(c)).

3. FOREIGN TRANSMITTAL LICENSE INFORMATION

Completed by:

[Signature]



Additional license for foreign transmittal not required. This subject matter is covered by a license already granted on the equivalent U.S. national application. Refer to that license for information concerning its scope.



License for foreign transmittal not required. 37 CFR 5.11(e)(1) or 37 CFR 5.11(e)(2). However, a license may be required for additional subject matter. See 37 CFR 5.15(b).



Foreign transmittal license granted. 35 U.S.C. 184; 37 CFR 5.11 on 3-4-00

(date)



37 CFR 5.15(a)



37 CFR 5.15(b)

Name and mailing address of the receiving Office
Assistant Commissioner for Patents
Box PCT
Washington, D.C. 20231

Attn: RO/US

Facsimile No.

Authorized officer

Telephone No.

Form PCT/RO/105 (July 1992)

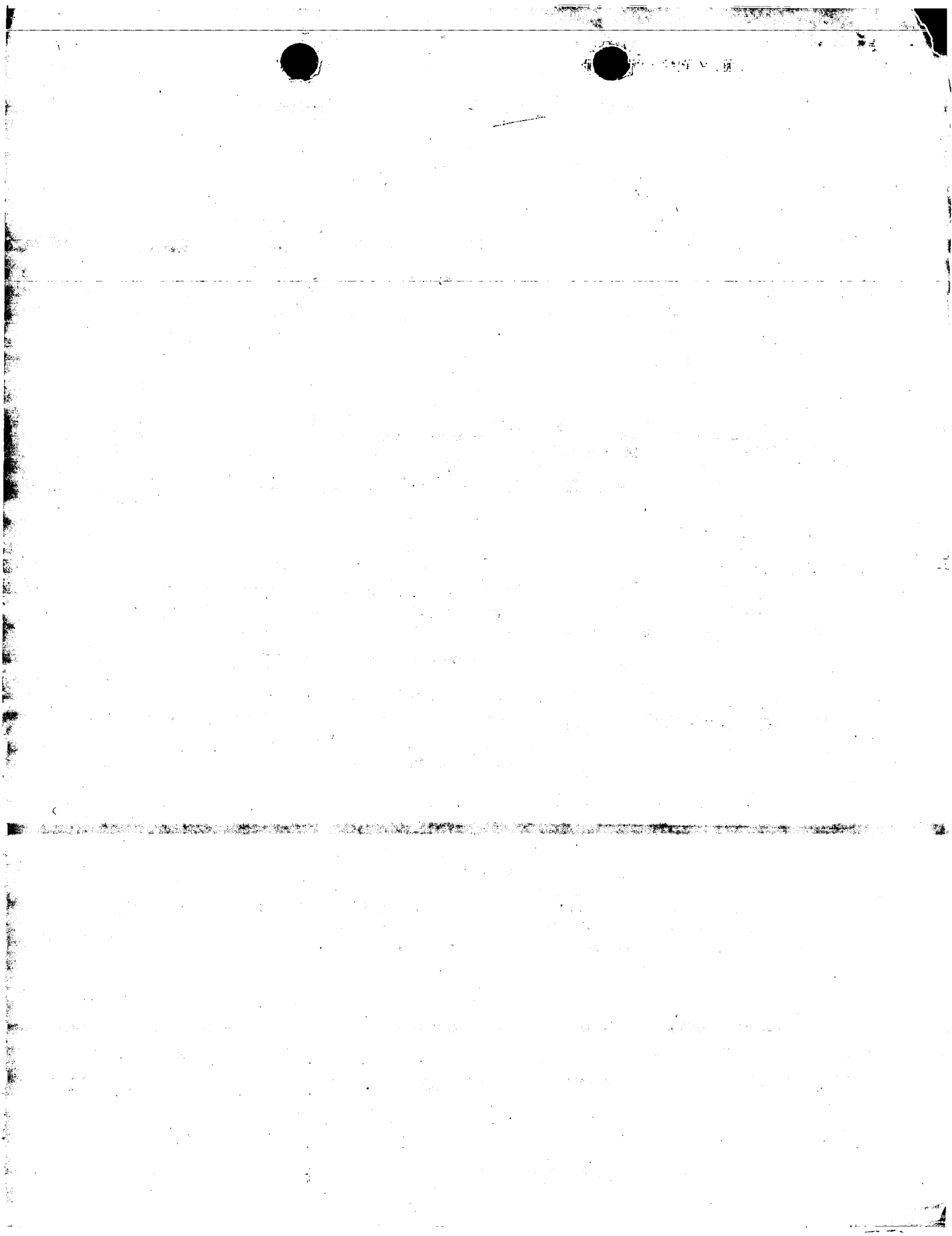
Tax

BL MAR 24 2000

Register

BL MAR 24 2000

MARK A. HOGARTH
INTERNATIONAL DIVISION
703-385-3749



PCT COOPERATION TREATY

RJP

PCT

From the INTERNATIONAL BUREAU

NOTICE INFORMING THE APPLICANT OF THE COMMUNICATION OF THE INTERNATIONAL APPLICATION TO THE DESIGNATED OFFICES

(PCT Rule 47.1(c), first sentence)

To:

PECHMAN, Robert, J.
Minnesota Mining and Manufacturing
Company
Office of Intellectual Property
Counsel
P.O. Box 33427
Saint Paul, MN 55133-3427
ETATS-UNIS D'AMERIQUE

REFERRED TO

Date of mailing (day/month/year) 05 October 2000 (05.10.00)		IMPORTANT NOTICE	
Applicant's or agent's file reference 54769PCT1A 003			
International application No. PCT/US00/03953	International filing date (day/month/year) 16 February 2000 (16.02.00)	Priority date (day/month/year) 25 March 1999 (25.03.99)	
Applicant MINNESOTA MINING AND MANUFACTURING COMPANY et al			

1. Notice is hereby given that the International Bureau has communicated, as provided in Article 20, the international application to the following designated Offices on the date indicated above as the date of mailing of this Notice:
AU, KP, KR, US

In accordance with Rule 47.1(c), third sentence, those Offices will accept the present Notice as conclusive evidence that the communication of the international application has duly taken place on the date of mailing indicated above and no copy of the international application is required to be furnished by the applicant to the designated Office(s).

2. The following designated Offices have waived the requirement for such a communication at this time:
AE, AL, AM, AP, AT, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EA, EE, EP, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, OA, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW
The communication will be made to those Offices only upon their request. Furthermore, those Offices do not require the applicant to furnish a copy of the international application (Rule 49.1(a-bis)).

3. Enclosed with this Notice is a copy of the international application as published by the International Bureau on 05 October 2000 (05.10.00) under No. WO 00/58990

REMINDER REGARDING CHAPTER II (Article 31(2)(a) and Rule 54.2)

If the applicant wishes to postpone entry into the national phase until 30 months (or later in some Offices) from the priority date, a demand for international preliminary examination must be filed with the competent International Preliminary Examining Authority before the expiration of 19 months from the priority date.

It is the applicant's sole responsibility to monitor the 19-month time limit.

Note that only an applicant who is a national or resident of a PCT Contracting State which is bound by Chapter II has the right to file a demand for international preliminary examination.

REMINDER REGARDING ENTRY INTO THE NATIONAL PHASE (Article 22 or 39(1))

If the applicant wishes to proceed with the international application in the national phase, he must, within 20 months or 30 months, or later in some Offices, perform the acts referred to therein before each designated or elected Office.

For further important information on the time limits and acts to be performed for entering the national phase, see the Annex to Form PCT/IB/301 (Notification of Receipt of Record Copy) and Volume II of the PCT Applicant's Guide.

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland Facsimile No. (41-22) 740.14.35	Authorized officer J. Zahra Telephone No. (41-22) 338.83.38
--	---

Se	W	Da	Hi	HP	ME	TW	JH	KB
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16 NOV. 2000

PATENT COOPERATION TREATY

From the INTERNATIONAL BUREAU

To:

HILLERINGMANN, Jochen
Bahnhofsvorplatz 1 (Deichmanhaus)
50667 Cologne
ALLEMAGNE

INFORMATION CONCERNING ELECTED
OFFICES NOTIFIED OF THEIR ELECTION

(PCT Rule 61.3)

Date of mailing (day/month/year) 07 November 2000 (07.11.00)		IMPORTANT INFORMATION	
Applicant's or agent's file reference 54769PCT1A			
International application No. PCT/US00/03953	International filing date (day/month/year) 16 February 2000 (16.02.00)	Priority date (day/month/year) 25 March 1999 (25.03.99)	
Applicant MINNESOTA MINING AND MANUFACTURING COMPANY et al			

1. The applicant is hereby informed that the International Bureau has, according to Article 31(7), notified each of the following Offices of its election:

AP : GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW

EP : AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE

National : AU, BG, CA, CN, CZ, DE, IL, JP, KP, KR, MN, NO, NZ, PL, RO, RU, SE, SK, US

2. The following Offices have waived the requirement for the notification of their election; the notification will be sent to them by the International Bureau only upon their request:

EA : AM, AZ, BY, KG, KZ, MD, RU, TJ, TM

OA : BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG

National : AE, AL, AM, AT, AZ, BA, BB, BR, BY, CH, CR, CU, DK, DM, EE, ES, FI, GB, GD, GE, GH,
GM, HR, HU, ID, IN, IS, KE, KG, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MW, MX, PT, SD,
SG, SI, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW

3. The applicant is reminded that he must enter the "national phase" before the expiration of 30 months from the priority date before each of the Offices listed above. This must be done by paying the national fee(s) and furnishing, if prescribed, a translation of the international application (Article 39(1)(a)), as well as, where applicable, by furnishing a translation of any annexes of the international preliminary examination report (Article 36(3)(b) and Rule 74.1).

Some offices have fixed time limits expiring later than the above-mentioned time limit. For detailed information about the applicable time limits and the acts to be performed upon entry into the national phase before a particular Office, see Volume II of the PCT Applicant's Guide.

The entry into the European regional phase is postponed until 31 months from the priority date for all States designated for the purposes of obtaining a European patent.

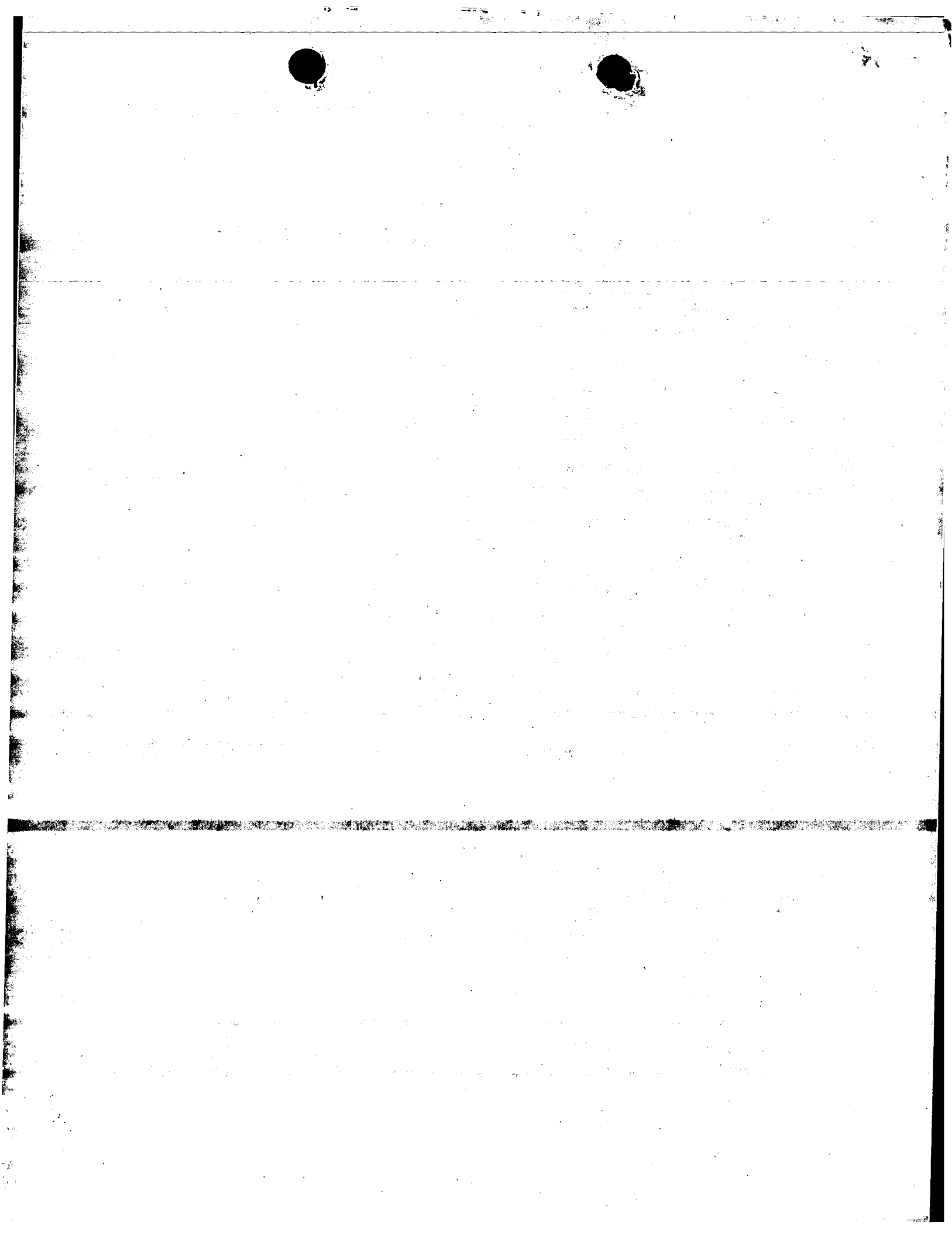
The International Bureau of WIPO
34, chemin des Colombettes
1211 Geneva 20, Switzerland

Facsimile No. (41-22) 740.14.35

Authorized officer:

Juan Cruz

Telephone No. (41-22) 338.83.38



PATENT COOPERATION TREATY

From the:
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

To:

HILLERINGMANN, Jochen
Patent Attorney
Bahnhofsvorplatz 1
(Deichmannhaus)
D-50667 Köln
ALLEMAGNE

Av	K	S	g	W	O	a	M	I	P	M	E	T	W	J	H	K	B
04. JAN. 2001																	
K F 0 2 . 0 4 . 0 1																	

PCT

WRITTEN OPINION

(PCT Rule 66)

Date of mailing
(day/month/year) 03.01.2001

Applicant's or agent's file reference
Hi-bu 001969wo

REPLY DUE within 3 month(s)
from the above date of mailing

International application No.
PCT/US00/03953

International filing date (day/month/year)
16/02/2000

Priority date (day/month/year)
25/03/1999

International Patent Classification (IPC) or both national classification and IPC
H01J9/24

Applicant
MINNESOTA MINING AND MANUFACTURING COMPANY et al.

1. This written opinion is the first drawn up by this International Preliminary Examining Authority.

2. This opinion contains indications relating to the following items:

- I ☒ Basis of the opinion
- II ☐ Priority
- III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- IV ☐ Lack of unity of invention
- V ☒ Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI ☐ Certain document cited
- VII ☒ Certain defects in the international application
- VIII ☒ Certain observations on the international application

3. The applicant is hereby invited to reply to this opinion.

When? See the time limit indicated above. The applicant may, before the expiration of that time limit, request this Authority to grant an extension, see Rule 66.2(d).

How? By submitting a written reply, accompanied, where appropriate, by amendments, according to Rule 66.3. For the form and the language of the amendments, see Rules 66.8 and 66.9.

Also: For an additional opportunity to submit amendments, see Rule 66.4.
For the examiner's obligation to consider amendments and/or arguments, see Rule 66.4 bis.
For an informal communication with the examiner, see Rule 66.6.

If no reply is filed, the international preliminary examination report will be established on the basis of this opinion.

4. The final date by which the international preliminary examination report must be established according to Rule 69.2 is: 25/07/2001.

Name and mailing address of the international preliminary examining authority:



European Patent Office
D-80298 Munich
Tel. +49 89 2399 - 0 Tx: 523656 epmu d
Fax: +49 89 2399 - 4465

Authorized officer / Examiner

Meul, H

Formalities officer (incl. extension of time limits)
Schuster-Kaechele, W
Telephone No. +49 89 2399 2281





WRITTEN OPINION

International application No. PCT/US00/03953

I. Basis of the opinion

1. This opinion has been drawn on the basis of (*substitute sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this opinion as "originally filed"*):

Description, pages:

1-10 as originally filed

Claims, No.:

1-9 as originally filed

Drawings, sheets:

1/2-2/2 as originally filed

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
- ☐ the language of publication of the international application (under Rule 48.3(b)).
- ☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- ☐ contained in the international application in written form.
- ☐ filed together with the international application in computer readable form.
- ☐ furnished subsequently to this Authority in written form.
- ☐ furnished subsequently to this Authority in computer readable form.
- ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

- ☐ the description, pages:
- ☐ the claims, Nos.:

WRITTEN OPINION

International application No. PCT/US00/03953

- ☐ the drawings, sheets:
5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):
(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)

6. Additional observations, if necessary:

V. Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement
- | | | |
|-------------------------------|--------|-----|
| Novelty (N) | Claims | 7 |
| Inventive step (IS) | Claims | 7-9 |
| Industrial applicability (IA) | Claims | |

2. Citations and explanations
see separate sheet

VII. Certain defects in the international application

The following defects in the form or contents of the international application have been noted:
see separate sheet

VIII. Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:
see separate sheet



R I t m V

R asoned statement under Rule 66.2 (a) (ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Reference is made to the following documents:

D1: WO 99/10909 A and corresponding EP 0 935 275 A1

D2: EP 0 196 033 A2 (copy attached)

2. The subject-matter of claim 7 does not meet the requirements of the PCT in respect of novelty and/or inventive step, the reasons being as follows:

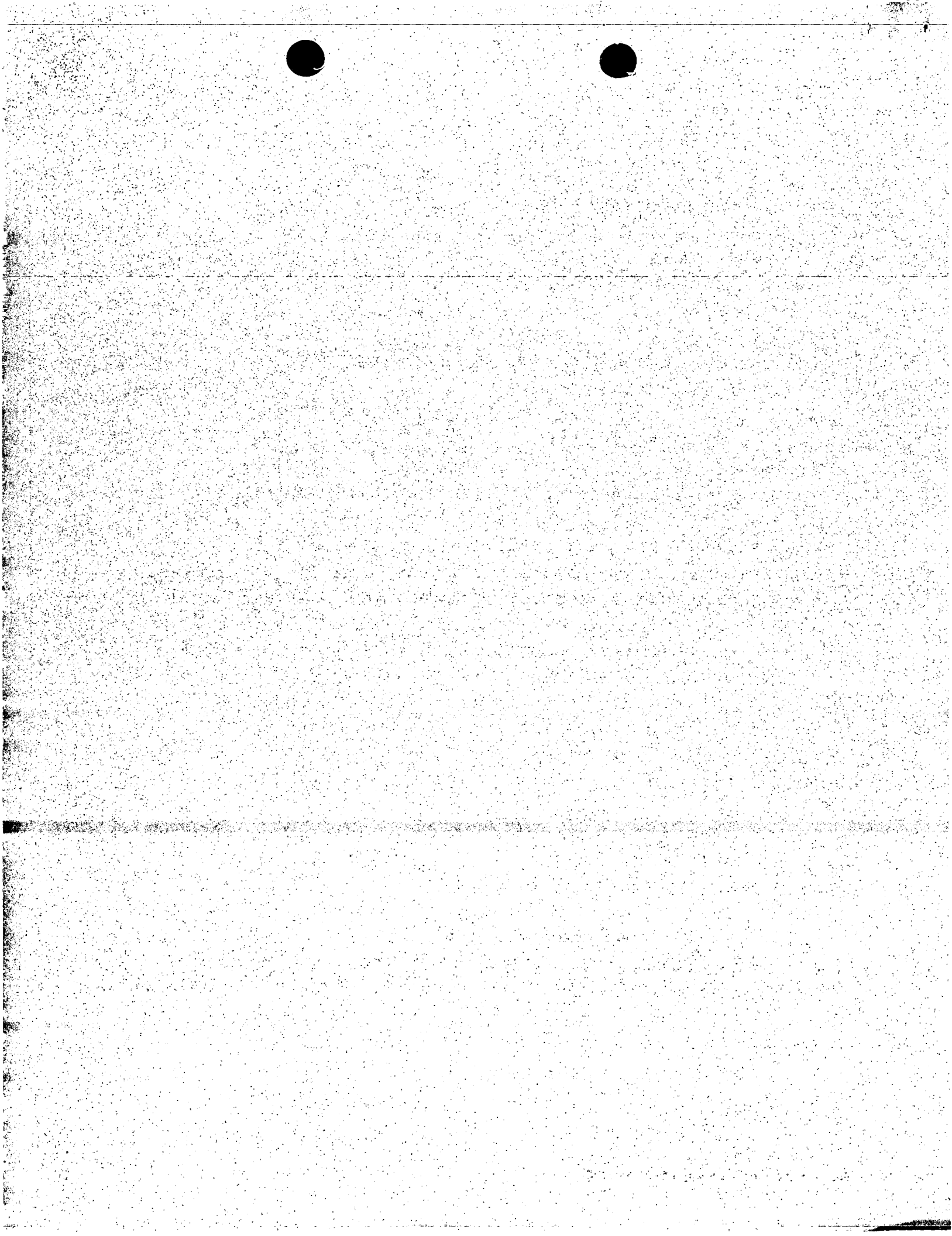
Claim 7 is not clear (see section VIII of this written opinion). The mould as such must not be defined by features which depend on the particular use of this mould. In order to assess novelty and inventive step of claim 7, features such as 'photo-setting initiator having an absorption edge whose wavelength is shorter than a wavelength corresponding to said first absorption edge of said first photo-setting initiator' are therefore neglected.

Consequently, the mould according to claim 7 is only defined by being a mould for fabricating a plasma display panel comprising a base and a rib, which mould is obtained by photo-setting a photo-setting component in the presence of a photo-setting initiator.

However, such a mould is not novel (see e.g. p. 5, l. 31-34 of D1) or at least strongly suggested for the following reasons:

A mould formed of silicone for fabricating a plasma display panel comprising a base and a rib is known from D1 (see Example 9 of D2).

A person skilled in the art of mould fabrication knows various mould fabrication processes including the photofabrication of master relief patterns as disclosed in D2 (see Figs. 3-7 and related text of D2). The material used for forming this master comprises a photo-setting component and a photo-setting initiator (see p. 10, l. 5 to p. 12, l. 7 and p. 15, l. 1 to p. 17, l. 4 of D2). Therefore, a skilled person



knowing the documents D1 and D2 would arrive at the mould as defined in claim 7 without the exercise of inventive skill.

3. Dependent claims 8-9 do not contain any features which, in combination with the features of claim 7 to which they refer, meet the requirements of the PCT in respect of inventive step (see e.g. p. 4, l. 14-34 of D2).
4. The applicant is invited to file new claims which take account of the above comments and the comments made in section VIII below.
The applicant should also indicate in the letter of reply the difference of the subject-matter of the new claim vis-à-vis the state of the art and the significance thereof.
In order to facilitate the examination of the conformity of the amended application with the requirements of Article 34 (2) (b) PCT, the applicant is requested to clearly identify the amendments carried out, no matter whether they concern amendments by addition, replacement or deletion, and to indicate the passages of the application as filed on which these amendments are based (see also Rule 66.8(a) PCT).
When filing amended claims the applicant should at the same time bring the description into conformity with the amended claims.

Re Item VII

Certain defects in the international application

1. The unit 'cps' employed on page 6 is not additionally expressed in terms of the unit stipulated by Rule 10.1 PCT.
2. Contrary to the requirements of Rule 5.1 (a) (ii) PCT, the relevant background art disclosed in the documents D1 and D2 is not mentioned in the description, nor are these documents identified therein.

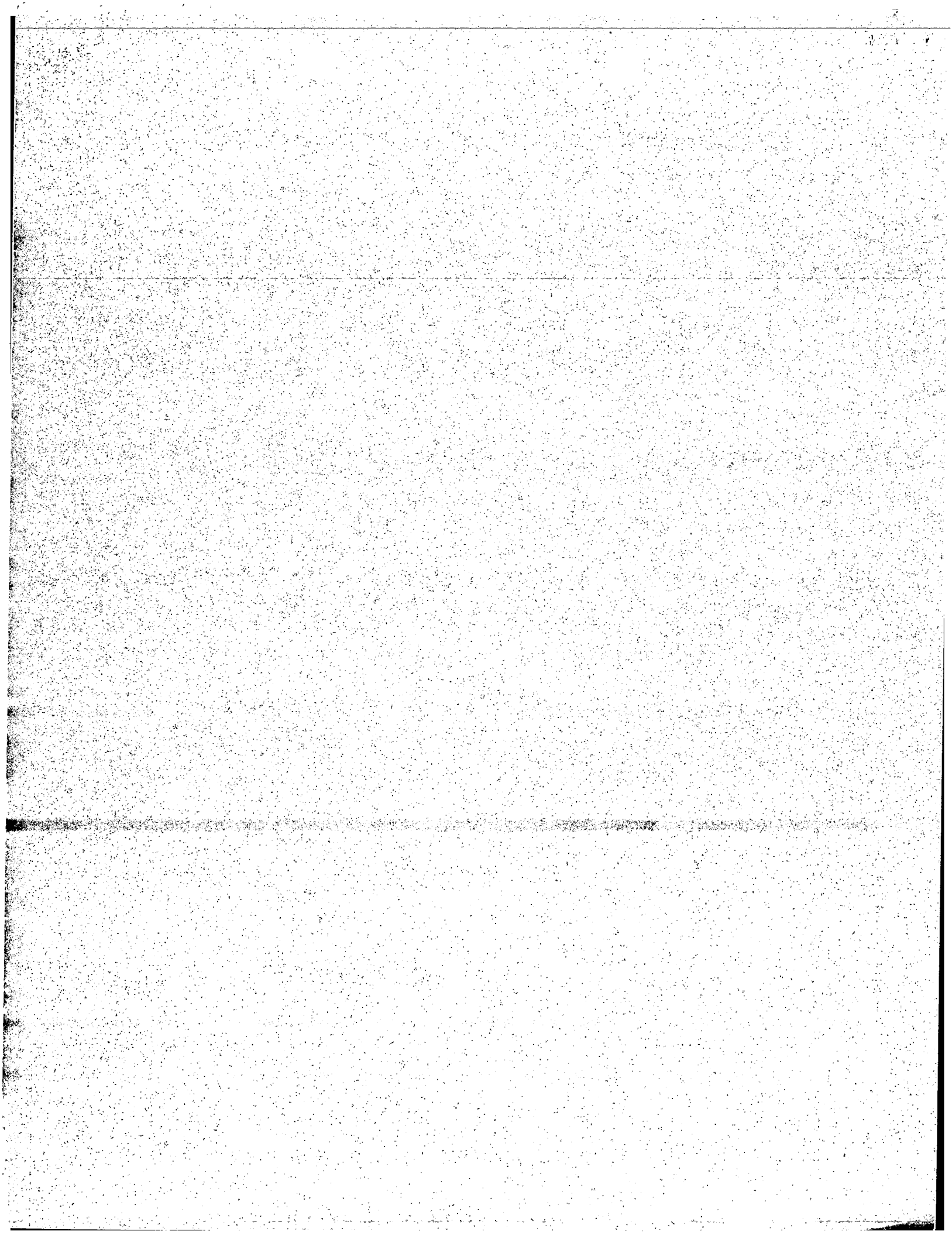
Re It m VIII

Certain observations on the international application

1. A lack of clarity arises in claim 1 because the step of 'contacting a rib precursor containing a first photo-setting initiator ... closely with said base' has to be carried out after the step of 'filling a mould ... with said rib precursor' (see present Figs. 2A-2C as well as p. 6, l. 28 to p. 7, l. 12 and Example 1). This processing step order is not clearly recited in claim 1 (Article 6 PCT).

A further lack of clarity arises in claim 1 because the difference between the terms 'substrate' and 'base' both used in the claim is unclear. A consistent terminology should be used throughout the whole application (Rule 10.2 PCT).

2. A lack of clarity arises in claim 7 because the claim does not define its subject-matter only in terms of technical features of the mould as such. On the contrary, features which depend on the particular use of this mould are used for the definition of the mould. For example, the feature 'photo-setting initiator having an absorption edge whose wavelength is shorter than a wavelength corresponding to said first absorption edge of said first photo-setting initiator' is not a clear and distinguishing feature of the mould; instead, it depends on the material to be filled into the recesses of the mould.
The intended limitations for the mould are therefore not clear from claim 7 (Article 6 PCT).



(19)



Europäisches Patentamt

European Patent Office

Office européen des brevets

(11)

Publication number:

0 196 033**A2**

(12)

EUROPEAN PATENT APPLICATION

(21) Application number: 85103949.3

(51) Int. Cl.: G 03 F 7/20, G 03 F 7/26

(22) Date of filing: 22.03.86

(30) Priority: 26.03.85 US 716096

(71) Applicant: E.I. DU PONT DE NEMOURS AND COMPANY,
1007 Market Street, Wilmington Delaware 19898 (US)(43) Date of publication of application: 01.10.86
Bulletin 86/40(72) Inventor: Wojcik, Michael S., 503 Cabot Drive, Hockessin
Delaware 19707 (US)

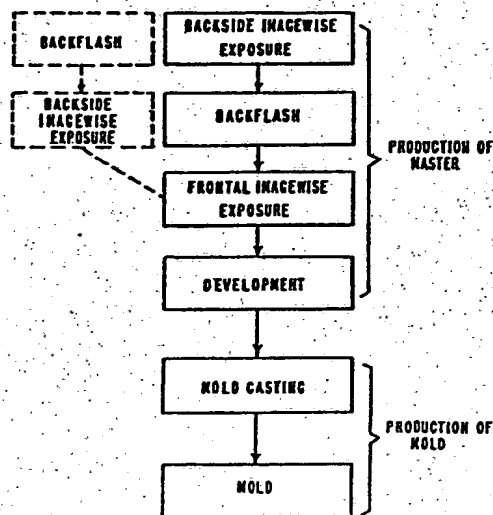
(84) Designated Contracting States: DE FR GB IT NL SE

(74) Representative: Werner, Hans-Karsten, Dr. et al,
Delchmannhaus am Hauptbahnhof, D-5000 Köln 1 (DE)

(54) Multilevel imaging of photopolymer relief layer for the preparation of casting molds.

(57) Process for photofabricating master relief patterns from photohardenable layers, e.g., 0.01 to 0.5 inch (0.25 to 12.7 mm in thickness) which comprises: (1) exposing the layer through the back surface to first imagewise modulated actinic radiation for time to render layer insoluble to first preselected depth which when measured from back surface is less than layer thickness, (2) exposing overall to actinic radiation through back to render layer insoluble to second preselected depth which when measured from back surface is less than first preselected depth, (3) exposing imagewise through front surface to actinic radiation for a time sufficient to render exposed areas of layer insoluble to depth extending from front surface to at least second preselected depth, and (4) solvent removing soluble areas of layer.

The master relief pattern is useful in making casting molds.



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TITLE

MULTILEVEL IMAGING OF PHOTOPOLYMER RELIEF
LAYER FOR THE PREPARATION OF CASTING MOLDS

DESCRIPTION

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TECHNICAL FIELD

This invention relates to a process for fabricating male patterns used to make casting molds. More particularly, this invention relates to a process for making male patterns used to make casting molds by photofabrication.

BACKGROUND ART

In the fabrication of decorative or commemorative plaques and the like, a female mold is usually prepared into which bronze or other metal is poured to produce a plaque having a raised inscription and/or design. Commemorative or decorative signs and plaques produced by cast metal, especially bronze, tend to have a rough and generally unappealing surface texture. While the top surface of the raised portions may be easily polished, the recessed background areas cannot be polished unless one goes to great expense to grind off the surface of the background areas using specialized equipment. It has been, therefore, common practice in the industry, to prepare a mold which reproduces a textured surface as background, such surface usually being a likeness of a leather pattern.

To prepare a mold, one must first make a three-dimensional male pattern which is basically a duplicate of the finished product. Typically, a leather-textured sheet is first attached to a wooden support to provide the needed background texture. Then any decorative patterns are glued over the textured surface or in place of sections of the textured surface. Decorative patterns involving

intricate lace-like work are also very hard to reproduce in the mold and are usually first hand-carved or etched and then attached to the remaining art work used in the making of the mold.

5 Finally, the lettering or other pattern is glued over the textured surface in the form of a three-dimensional carving. Once a satisfactory master relief pattern has been assembled, a mixture of wax and sand as is known to those skilled in the art is poured over the pattern to form a female mold

10 of the pattern of the original art work. The master pattern is later removed and metal, e.g., bronze, silver, copper, etc. cast in the mold to replicate the master pattern.

15 As is readily understood, accurate reproduction of the original art work in the making of the male pattern is both difficult and expensive. It is therefore desirable to develop a process where artwork of intricate relief patterns can be

20 accurately reproduced at low cost by a quick, relatively fast procedure.

BRIEF DESCRIPTION OF THE DRAWING

In the accompanying drawing forming a material part of this disclosure:

25 Figure 1 is a block diagram of the steps required to prepare a master relief pattern designated "Master" in accordance with the invention and a mold from the master.

30 Figure 2 shows in schematic presentation a portion of a typical decorative plaque prepared in accordance with the invention.

Figure 3 is a schematic presentation of a side view of a photohardenable element useful in practicing this invention.

Figures 4 through 6 illustrate schematically the effect of the exposure steps used to prepare a master for the preparation of a casting mold in accordance with this invention.

5 Figure 7 is a schematic illustration of a master prepared by the invention, and

Figures 8 and 9 show schematically the use of the master for the preparation of a casting mold.

DISCLOSURE OF THE INVENTION

10 In accordance with this invention there is provided a process for photofabricating master relief patterns for the production of casting molds using a photohardenable, solvent soluble layer having a front and a back surface and a thickness in the range of
15 0.010 to 0.5 inch (0.25 to 12.7 mm), comprising the steps of:

- 20 (1) exposing the layer through the back surface to a first imagewise modulated actinic radiation for a predetermined duration selected to penetrate the layer and render it imagewise insoluble to a first preselected depth which measured from the back surface is less than the total thickness of the photohardenable layer.
25
- (2) exposing the layer a second time through the back surface to unmodulated actinic radiation for a time sufficient to render insoluble the photohardenable
30 layer to a second preselected depth which measured from the back surface is less than the first preselected depth.
- (3) exposing the layer through the front surface to a second imagewise modulated
35 actinic radiation, for a time sufficient

t render insoluble the photohardenable layer to a depth extending from the front surface to at least said second preselected depth, and

- 5 (4) subjecting the layer to the action of a solvent to remove any portions of the layer not rendered solvent insoluble in steps (1) through (3).

10 As used herein the word "solvent" means any fluid capable of dissolving unhardened photohardenable material, including organic solvents, aqueous solutions, or mixtures thereof.

DETAILED DESCRIPTION OF THE INVENTION

15 In the photofabricating of master relief patterns hereinafter designated "master" for the subsequent production of casting molds there is utilized a single layer of a photohardenable composition comprising a polymer of a conjugated diolefin hydrocarbon, a nongaseous, ethylenically
20 unsaturated compound, an organic, radiation-sensitive, free-radical generating photoinitiator or system as well as other additives discussed below. The compositions may be used in layer form or the layer may be adhered to flexible supports, or a
25 temporary support may be used. Another configuration may have a cover sheet and polymeric layer on each side of the photosensitive layer. Preferably the support and/or cover sheet are transparent to actinic radiation used to expose the photohardenable layer as
30 described more fully below. The support and cover sheet are generally as thin as possible so that in the event they are present during exposure the scattering of actinic radiation will be kept to a minimum. Non-transparent supports or cover sheets,
35 of course, must be removed prior to exposure to

actinic radiation without damaging the photohardenable layer. The preferred support and cover sheet are removed prior to said exposure. Useful supports and cover sheets include plastic films, e.g., polyethylene terephthalate, polyvinyl chloride, polyamide, polyurethane, etc. To aid in removal of the support and cover sheet they are treated with release agents such as silicone or other known release agents.

10 The process of this invention as described above is illustrated in the block diagram shown in Figure 1. Generally the first exposure is a backside
15 imagewise exposure followed by an overall exposure through the backside designated "Backflash" and
20 frontal imagewise exposure through a phototool, e.g., image-bearing transparency or mask which bears the image or design desired. As shown by the broken blocks the order of exposure through the backside can be reversed, i.e., the backflash can occur first
25 followed by a backside imagewise exposure. After the exposure the unhardened areas of the layer are removed by solvent development to form the master. The master is then used in mold casting whereby a mixture of mold-making material, e.g., comprising
30 sand and wax as known to those skilled in the art, is packed over the master to replicate a complementary relief pattern, and, following removal of the master, a female mold results which is suitable for casting of a metal decorative plaque or other article.

30 In more detail, Figure 2 shows a portion of a typical decorative plaque 10 prepared by the process intended for use in a banking establishment. The plaque typically prepared from bronze comprises a background portion 15 containing a decorative
35 leather-like textured pattern 16. The plaque may be

surrounded by a raised border 12. The plaque will further contain raised letters 14 and/or a decorative design not shown. In order to produce such a plaque, molten bronze or other known casting metals, e.g., silver, aluminum, gold, platinum, copper, etc. is cast into a mold containing a complementary recessed pattern of the raised pattern found in the plaque.

The photohardenable layer useful in the practice of the invention is formed from a composition, a polymer of a conjugated diolefin hydrocarbon, an ethylenically unsaturated compound and an initiator activatable by actinic radiation. The photohardenable layer is developable in its unexposed state in aqueous, semiaqueous basic, or organic solvent solutions depending on the particular polymeric binder or binders present therein. The layers are in a thickness range of about 0.010 to 0.500 inch (about 0.25 to 12.7 mm) or more.

Suitable binders include natural or synthetic polymers of conjugated diolefin hydrocarbons. Examples of the binders include: 1,2-polybutadiene, 1,4-polybutadiene, butadiene/acrylonitrile, butadiene/styrene, block copolymers of the A-B-A type, e.g., styrene-butadiene-styrene block copolymer, styrene-isoprene-styrene block copolymer, etc., and copolymers of the binders. The block copolymers may be of the linear, radial, or sequential type. Also useful are block copolymers of the A-B-C type which have A and B blocks and a C block of a random copolymer of the A and B components or other components. Such copolymers are disclosed in Heinz et al., U.S. Patent 4,328,188, which is incorporated herein by reference. The preferred binders are the styrene-isoprene-styrene or styrene-butadiene-styrene

block copolymers and butadiene/acrylonitril copolymers optionally having a carboxyl content.

Useful linear block copolymers of this invention have at least one unit of the general formula, A-B-A, wherein each A is an independently selected nonelastomeric polymer block having a number average molecular weight (\bar{M}_n) of 2000-100,000 and a glass transition temperature above 25°C and B is an elastomeric polymer block having an average molecular weight between about 25,000 and 1,000,000 and a glass transition temperature below about 10°C. The nonelastomeric blocks, A, having between them an elastomeric block, B, together comprise the unit A-B-A which represents the copolymers uniquely suitable for use in combination with the photopolymerizable components in the compositions of the invention. This unit may comprise the entire general formula of the copolymer; it may be appended to another polymer chain; or it may be repeating. It is, of course, possible to vary the precise nature of the unit within the scope of the invention, e.g., by using two different nonelastomeric terminal blocks, A, or by creating block or graft polymeric substitutions in blocks A and B. Preferably, the elastomeric mid-section blocks, B, are polymers of aliphatic conjugated diolefins while the nonelastomeric blocks, A, are those formed by polymerizing alkenyl aromatic hydrocarbons, preferably vinyl substituted aromatic hydrocarbons, and still more preferably vinyl monocyclic aromatic hydrocarbons. The block copolymers are disclosed in Holden et al. U.S. Patent 3,265,765 and counterpart British Patent 1,000,090, incorporated herein by reference. Particularly preferred species of the subject copolymers comprise block copolymers f

polystyrene terminal groups connected by a mid-section of polyisoprene or polybutadiene, e.g., polystyrene-polyisoprene-polystyrene or polystyrene-polybutadiene-polystyrene, the polydiene block being 70 to 90% by weight of the block copolymer. Other typical block copolymers useful in this invention are polystyrene-polybutadiene-polystyrene and polystyrene-polyisoprene-polystyrene block copolymers which have been hydrogenated according to the teachings of Jones, U.S. Patent 3,431,323 and Hefelet al., U.S. Patent 3,333,024. The hydrogenated block copolymers have the additional advantage of improved thermal and oxidative resistance. However, some residual unsaturation in hydrogenated block copolymers is undesirable, since only very small concentrations of monomer are then needed in the photosensitive compositions to reduce solvent solubility upon exposure to actinic radiation. Still other typical block copolymers useful in this invention are those wherein the terminal blocks are polyalkyl styrenes, e.g., poly(α -methyl styrene)-polyisoprene-poly(α -methyl styrene), and those composed of a plurality of polymer blocks, e.g., polyisoprene-polystyrene-polybutadiene-polystyrene-polyisoprene.

The number average molecular weights for the block copolymers can be determined by membrane osmometry utilizing a gel cellophane 600 W membrane manufactured by Arro Laboratories, Inc., Joliet, IL and toluene as the solvent at 29°C. The \bar{M}_n for the nonelastomeric polymer blocks and elastomeric polymer blocks are preferably determined as follows:

A. The molecular weight of the first block (polystyrene) can be measured by gel permeation chromatography (GPC) of a terminated sample removed.

immediately after the polymerization. The chromatograph is calibrated using commercially available polystyrene molecular weight standards.

5 B. The \bar{M}_n of the second block (polyisoprene or polybutadiene) can be determined in the following manner:

(1) measuring by suitably calibrated GPC the \bar{M}_n of a sample of polystyrene-polyisoprene (or polybutadiene) diblock polymer terminated and removed immediately after its polymerization, and (2) subtracting from this value the \bar{M}_n of the first block as determined in (A) above.

C. The \bar{M}_n of the third block (polystyrene) can be determined in the same general manner:

15 (1) measuring by suitably calibrated GPC the \bar{M}_n of the sample of polystyrene-polyisoprene (or polybutadiene)-polystyrene triblock polymer, and (2) subtracting from this value the \bar{M}_n of the diblock polymer obtained in (B) above. The block copolymers are manufactured by Shell Chemical Company and sold under the trademark "Kraton®".

Useful butadiene/acrylonitrile copolymers are high molecular weight butadiene/acrylonitrile copolymers having a number average molecular weight (25 \bar{M}_n) in the range of about 20,000 to about 75,000, preferably in the range of about 25,000 to about 50,000. The \bar{M}_n for the polymers described herein can be determined by gel permeation chromatography employing a polybutadiene standard. The acrylonitrile content of the polymers varies from about 10 to about 50% by weight, preferably from about 15 to about 40%. Optionally, the copolymer also has a carboxyl content of 0 to about 15% by weight. When the copolymer contains carboxyl groups, 35 the carboxyl content is preferably in the range of

about 1 to about 15%, most preferably in the range of about 2 to about 10% by weight. The copolymer is present in an amount of about 55 to 90% by weight, based on the total weight of the composition, and preferably about 60 to about 75% by weight. At least about 55% by weight of the copolymer is necessary to give adequate flexibility and physical integrity to the photosensitive elements, particularly for flexographic plates.

Carboxyl groups may be incorporated into the high molecular weight copolymer by addition to the polymerization process of a carboxyl containing monomer, e.g., acrylic or methacrylic acid, or a monomer which is convertible to a carboxyl containing group, e.g., maleic anhydride or methyl methacrylate. Such polymers are available commercially from several sources, e.g., from the B. F. Goodrich Chemical Company under the trade name Hycar®.

Another essential ingredient of the photosensitive compositions of this invention is a nongaseous, ethylenically unsaturated compound, preferably containing at least one terminal ethylenic group. These compounds generally are capable of forming a high polymer by free-radical initiated chain-propagating addition polymerization and be compatible with the high molecular weight polymers described above. Ethylenically unsaturated compounds which are compatible with the A-B-A type block copolymers set forth above are disclosed in British Patent 1,366,769 incorporated herein by reference. Many of these monomers are specifically disclosed below. One class of suitable ethylenically unsaturated compounds includes unsaturated esters of alcohols, especially such esters of α -methylene

carboxylic acids and substituted α -methylene carboxylic acids, more especially such esters of alkylene polyols and polyalkylene polyols, and most especially alkylene polyol di- and tri-acrylates and

5 polyalkylene polyol di- and tri-acrylates prepared from alkylene polyols of 2-15 carbon atoms or polyalkylene ether polyols or glycols of 1-10 ether linkages.

The following specific compounds are further

10 illustrative of this class: ethylene glycol diacrylate, diethylene glycol diacrylate, glycerol diacrylate, glycerol triacrylate, trimethylolpropane triacrylate, ethylene glycol dimethacrylate, 1,3-propanediol dimethacrylate, 1,2,4-butanetriol

15 trimethacrylate, 1,4-cyclohexanediol diacrylate, 1,4-benzenediol dimethacrylate, 1,2-benzenedimethanol diacrylate, pentaerythritol triacrylate, pentaerythritol tetra-methacrylate, 1,3-propanediol diacrylate, 1,3-pentane-diol dimethacrylate,

20 p- α,α -dimethylbenzylphenyl acrylate, t-butyl acrylate, N,N-diethylaminoethyl acrylate, diethylaminoethyl methacrylate, 1,4-butane-diol diacrylate, hexamethylene glycol diacrylate, decamethylene glycol diacrylate,

25 2,2-dimethylolpropane diacrylate, tripropylene glycol diacrylate, 2,2-di(p-hydroxy-phenyl)propane diacrylate, 2,2-di(p-hydroxy-phenyl)propane dimethacrylate, polyoxyethyl-2,2-di(p-hydroxy-phenyl)propane triacrylate (molecular weight of 462),

30 1,4-butanediol dimethacrylate, hexamethylene glycol dimethacrylate, 2,2,4-trimethyl-1,3-pentanediol dimethacrylate, 1-phenylethylene-1,2-dimethacrylate, trimethylolpropane trimethacrylate, triethylene glycol diacrylate, ethylene glycol acrylate,

35 phthalate, polyoxyethyltrimethylolpropane

triacrylat, diacrylate and dimethacrylate esters of diepoxy polyethers derived from aromatic polyhydroxy compounds such as bisphenols, novolaks and similar compounds such as those described by Cray in U.S. Patent 3,661,576, which is incorporated by reference, the bis-acrylates and methacrylates of polyethylene glycols of molecular weight 200-500, etc.

Another class of suitable ethylenically unsaturated compounds includes the compounds disclosed by Martin and Barney in U.S. Patent 2,927,022 which is incorporated herein by reference, e.g., those having a plurality of addition polymerizable ethylenic linkages, particularly when present as terminal linkages, and especially those wherein at least one and preferably most of such linkages are conjugated with a double bonded carbon, including carbon double bonded to carbon and to heteroatoms such as nitrogen, oxygen and sulfur. Preferred are such materials wherein the ethylenically unsaturated groups, especially the vinylidene groups, are conjugated with ester or amide structures. Specific examples of such compounds include unsaturated amides, particularly those of α -methylene carboxylic acids, especially with α -omega-diamines and oxygen-interrupted omega-diamines, such as methylene bis-acrylamide, methylene bis-methacrylamide, ethylene bis-methacrylamide, 1,6-hexamethylene bis-acrylamide, diethylene triamin trimethacrylamide, bis(γ -methacrylamidopropoxy)-ethane, β -methacrylamidoethyl methacrylate, N-(β -hydroxyethyl)- β -(methacrylamido)ethyl acrylate, and N,N-bis(β -methacryloxyethyl) acrylamide; vinyl esters such as divinyl succinate, divinyl adipate, divinyl phthalate, divinyl terephthalate, divinyl benzene-1,3-disulfonate, and divinyl butan-1,4-disulfonate; diallyl fumarate; etc.

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Additional ethylenically unsaturated compounds which may be used include styrene and derivatives thereof: 1,4-diisopropenylbenzene, 1,3,5-triisopropenylbenzene; itaconic anhydride adducts with hydroxyethyl acrylate (1:1), itaconic anhydride adducts with liquid butadiene/acrylonitrile polymers containing terminal amino groups, and itaconic anhydride adducts with the diacrylate and dimethacrylate esters of diepoxy polyethers described in Cray U.S. Patent 3,661,576; polybutadiene and butadiene/acrylonitrile copolymers containing terminal and pendant vinyl groups; and unsaturated aldehydes, such as sorbaldehyde (2,4-hexadienal).

Ethylenically unsaturated compounds which are water soluble or contain carboxyl or other alkali-reactive groups are especially suitable when aqueous basic-developable systems are involved. In addition, the polymerizable, ethylenically unsaturated polymers of Burg, U.S. Patent 3,043,805; Martin, U.S. Patent 2,929,710; and similar materials may be used alone or mixed with other materials. Acrylic and methacrylic esters of adducts of ethylene oxide and polyhydroxy compounds such as those described by Cohen and Schoenthaler in U.S. Patent 3,380,831 are also useful. The photocrosslinkable polymers disclosed in Schoenthaler, U.S. Patent 3,418,295, and Celeste, U.S. Patent 3,448,089, may also be used. All of these patents are incorporated herein by reference.

The ratio of the weight of block copolymer used to the weight of addition polymerizable ethylenically unsaturated compound use is 99:1 to about 1:1.

The amount of unsaturated compound present in a photosensitive composition containing a butadiene/acrylonitrile copolymer should be in the

range of about 2 to about 40% by weight, based on the total weight of composition. The specific amount for optimum results will vary depending on the particular polymers used. Preferably the amount of unsaturated compound is in the range of about 5 to about 25%.

The ethylenically unsaturated compound preferably has a boiling point at normal pressure of over about 100°C. The most preferred ethylenically unsaturated compounds are triethylene glycol diacrylate, triethylene glycol dimethacrylate, hexamethylene glycol dimethacrylate and hexamethylene glycol diacrylate.

The photosensitive compositions of this invention substantially do not scatter actinic radiation when in the form of thin layers, as described above. In order to secure a substantially transparent mixture, i.e., a nonradiation-scattering mixture, the polymer binder components should be compatible with, and preferably soluble in, the ethylenically unsaturated compound in the proportions used.

By "compatible" is meant the ability of two or more constituents to remain dispersed in one another without causing any significant amount of scattering of actinic radiation. Compatibility is often limited by the relative proportions of the constituents, and incompatibility is evidenced by formation of haze in the photosensitive composition. Some slight haze can be tolerated from such compositions before or during exposure in the preparation of printing reliefs, but when fine detail is desired, haze should be completely avoided. The amount of ethylenically unsaturated compound, or any other constituent, used is therefore limited to those concentrations which do not produce undesirable light scatter or haze.

The photosensitive compositions also contain an organic, radiation-sensitive, free-radical generating system. Practically any organic, radiation-sensitive, free-radical generating system which initiates polymerization of the unsaturated compound and does not excessively terminate the polymerization can be used in the photosensitive compositions of this invention. The term "organic" is used here and in the claims to designate compounds which contain carbon, and one or more of oxygen, hydrogen, nitrogen, sulfur and halogen, but no metal. Because process transparencies transmit heat originating from conventional sources of actinic radiation, and since the photosensitive compositions are usually prepared under conditions resulting in elevated temperatures, the preferred free-radical generating compounds are inactive thermally below 85°C and more preferably below 185°C. They should be dispersible in the composition to the extent necessary for initiating the desired polymerization or cross-linking under the influence of the amount of radiation absorbed in relatively short term exposures. These initiators are useful in amounts from about 0.001 to about 10% by weight, and preferably from about 0.1 to about 5% based on the total weight of the solvent-free photosensitive composition.

The free-radical generating system absorbs radiation within the range of about 2000 to about 8000 Å and has at least one component that has an active radiation absorption band with molar extinction coefficient of at least about 50 within the range of about 2500 to about 8000 Å, and preferably about 2500 to about 5000 Å. The term "active radiation absorption band" means a band of

radiation which is active to produce the free radicals necessary to initiate polymerization or crosslinking of the unsaturated material.

The free-radical generating system can
 5 comprise one or more compounds which directly furnish free radicals when activated by radiation. It can also comprise a plurality of compounds, one of which yields the free radicals after having been caused to
 10 do so by a sensitizer which is activated by the radiation.

A large number of such free-radical generating compounds can be utilized in the practice of the invention and include aromatic ketones such as benzophenone, Michler's ketone [4,4'-bis(dimethyl-
 15 amino)benzophenone], 4,4'-bis(diethylamino)benzophenone, 4-acryloxy-4'-dimethylaminobenzophenone, 4-acryloxy-4'-diethylaminobenzophenone, 4-methoxy-4'-dimethylaminobenzophenone, 2-phenyl-2,2-dimethoxyacetophenone (2,2-dimethoxy-1,2-diphenyl ethanone),
 20 2-ethylanthraquinone, phenanthraquinone, 2-*t*-butylanthraquinone, 1,2-benzanthraquinone, 2,3-benzanthraquinone, 2,3-dichloronaphthoquinone, benzil dimethyl acetal, and other aromatic ketones; benzoin, benzoin ethers such as benzoin methyl ether, benzoin ethyl
 25 ether, benzoin isobutyl ether, and benzoin phenyl ether, methylbenzoin, ethylbenzoin and other benzoin; and 2,4,5-triarylimidazolyl dimers such as 2-(*o*-chlorophenyl)-4,5-diphenylimidazolyl dimer, 2-(*o*-chlorophenyl)-4,5-di(*m*-methoxyphenyl)imidazolyl
 30 dimer, 2-(*o*-fluorophenyl)-4,5-diphenylimidazolyl dimer, 2-(*o*-methoxyphenyl)-4,5-diphenylimidazolyl dimer, 2-(*p*-methoxyphenyl)-4,5-diphenylimidazolyl dimer, 2,4-di(*p*-methoxyphenyl)-5-phenylimidazolyl dimer, 2-(2,4-dimethoxyphenyl)-4,5-diphenylimidazolyl
 35 dimer, 2-(*p*-methylmethylcaptophenyl)-4,5-diphenylimid-

azolyl dimers, etc., as disclosed in U.S. Patents 3,479,185 and 3,784,557 and in British Patents 997,396 and 1,047,569. These patents are incorporated herein by reference.

- 5 The imidazolyl dimers can be used with a free-radical producing electron donor such as 2-mercaptobenzoxazole, Leuco Crystal Violet or tri(4-diethylamino-2-methylphenyl)methane. Such sensitizers as Michler's ketone may be added.
- 10 Various energy transfer dyes such as Rose Bengal and Eosin Y can also be used. Additional examples of suitable initiators are disclosed by Plambeck in U.S. Patent 2,760,863 which is incorporated herein by reference.
- 15 The photosensitive compositions may also contain a small amount of thermal addition polymerization inhibitor, e.g., 0.001% to 2.0%, based on the weight of the total solvent-free photosensitive composition. Suitable inhibitors
- 20 include hydroquinone and alkyl and aryl-substituted hydroquinones, 2,6-di-tert-butyl-4-methylphenol, p-methoxyphenol, tert-butylpyrocatechol, pyrogallol, 8-naphthol, 2,6-di-tert-butyl-p-cresol, phenothiazine, pyridine, nitrobenzene, dinitrobenzene
- 25 and the nitroso dimer inhibitor systems described in U.S. Patent 4,168,982 which is incorporated herein by reference. Other useful inhibitors include p-toluquinone, chloranil and thiazine dyes, e.g., Thionine Blue G (CI 52025), Methylene Blue B
- 30 (CI 52015) and Toluidine Blue (CI 52040). Such compositions can be photopolymerized or photocrosslinked without removal of the inhibitor. The preferred inhibitors are 2,6-di-tert-butyl-4-methylphenol and p-methoxyphenol.
- 35

Typically such a photohardenable layer 20 shown in Figure 3 comprises a supporting base 22 usually out of polyethylene terephthalate, preferably having a release coating, e.g., silicon, thereon. Over the photohardenable layer 20 is a removable cover sheet 24. Typical thickness of the photohardenable layer 20 is $D=0.112$ inch (2.85 mm). The layer has a front side 21 and a backside 19. It is preferable that a photohardenable layer used in this process has not had any prior exposure to actinic radiation from either the front or the backside. However, layers having received a preexposure to unmodulated radiation through the backside to form a relatively thin hardened lower portion of the layer may also be used.

The first step of the process involves the backside imagewise exposure of the photohardenable layer 20. This operation is best understood with reference to Figure 4. The layer is placed in an exposure unit, generally equipped with a vacuum frame, backside up, preferably with support 22 removed. The exposure unit has been omitted from the figures for simplicity. A source of actinic radiation 30 at a given distance from the exposure unit and the photohardenable layer is depicted. Actinic radiation 28 from the source is directed towards the layer. In the preferred embodiment it is desirable that the actinic radiation be collimated; usually a point source of light such as a NAPPS exposure unit may be used. This is desirable to prevent sidewise spread of the light and loss of resolution during the exposure process. Other known exposure sources are also useful; those rich in ultraviolet radiation are preferred. A light modulator which may consist of a transparency 26

having imagewise transparent 27 and opaqu 29 areas, preferably having a matte surface, is place over layer 20. The modulator 26 allows actinic radiation 28 to expose the photosensitive layer 20 in a pattern of a desired background, e.g., as a reproduction of textured leather.

The exposure time and the intensity of the actinic radiation 28 is calculated such as to render insoluble the portions 32 of the photohardenable layer 20 that are exposed to the radiation, to a depth d_1 preselected to correspond to the raised portions of the background level of the finished master. Typically d_1 is 0.040 to 0.050 inch (1.016 to 1.27 mm).

Following the first exposure, the modulator 26 is removed and the photohardenable layer is subjected to a second non-modulated back exposure as shown in Figure 5. This exposure known as backflash is calculated to render uniformly insoluble a layer 34 extending a second predetermined depth d_2 as measured from the backside 19 of the photosensitive layer 20. Typically d_2 is .010 to .020 inch (0.254 to 0.5 mm). As shown in Figure 5 this depth as measured from surface 19 is less than the depth d_1 to which the photohardenable layer has been rendered insoluble in an imagewise pattern by the first exposure. This determines how deep will be the relief of the background pattern. Typically this relief is about 0.030 inch (0.762 mm).

When layers that have received a non-image exposure through the back are used, (usually, but not necessarily during manufacturing) the backflash exposure step is not needed. However, care must be used in calculating the first exposure to provide a depth d_1 exc eding th d pth d_2 of insolubl layer produced by this unmodulat d backflash exposure.

The layer with cover sheet 24 is now taken out of the exposure station and the supporting base 22 replaced over the back surface 19 of the photohardenable layer 20. The plate is next placed back on the exposure station with frontside 21 now facing the actinic radiation source. The cover layer 24 is removed and a second modulator 36 which contains the art work representing the raised portions of the final plaque or article is placed over surface of front side 21. Again this modulator contains transparent 40 and opaque 38 areas corresponding to the art work. Again, the modulator can be a litho type transparency preferably having a matte surface. The photohardenable layer is now exposed to a second imagewise exposure for a preselected time sufficient to render it insoluble to a depth at least as great as $D - d_2$ as measured from the top surface of front side 21, i.e., the exposed areas will become insoluble through the entire thickness of the photohardenable layer. Hardened area 42 shows a depth of at least $D - d_2$.

Following this exposure, the layer is placed in a standard developing apparatus where under the action of solvent the soluble portions of the plate are washed away leaving a relief image on a base layer which replicates both the background pattern and the relief art work. The master 43 shown in Figure 7 is prepared after liquid development which may be used to produce a casting mold.

The making of a mold proceeds along the traditional casting mold making operations. As shown in Figure 8, a mixture of sand and wax of a composition known to those skilled in the art 44 is poured and pressed all around the relief portions of the master. The master is then removed leaving

5 It is within the contemplation of the present invention to employ a scanning light source, such as a scanning laser beam and combine such a source with an electro-optical or other similar modulator. While best results have been obtained
0 using the process step sequence discussed, the order of the three exposure steps may be altered provided that the various exposures are precalculated to render insoluble the photohardenable layer to depths as disclosed above.

A flexographic printing plate commercially available under the trade name Cyrel® 112SC (E. I. du Pont de Nemours and Company, Wilmington, DE) was first exposed to modulated actinic radiation in a commercial Cyrel® 3040 exposure unit comprising a bank of 24 U.V. fluorescent black light tube lamps made by Sylvania Co., type 7R-48T-12/B2/VHO/180. Prior to this exposure the polyethylene terephthalate film support was removed from the flexographic printing plate. The film was placed in the exposure unit with the uncovered side facing the exposure source. A matte surface litho-type negative such as the Cronar® Polyester Photographic Film (E. I. du Pont de Nemours and Company, Wilmington, DE) containing the pattern desired to be reproduced as background for a given plaque is placed over the plate. Vacuum was applied to provide good contact between the negative and the plate and the plate was exposed to actinic radiation for 12 seconds.

種

Photographic Film negative was removed and using the same exposure equipment the plate was exposed to actinic radiation for an additional 5 seconds. The plate was then removed from the exposure equipment and the polyethylene terephthalate film support readhered to the exposed surface of the plate. The cover sheet of the plate was next removed and the plate placed again in the exposure equipment stripped side up. A second litho negative of the same type as before bearing an image of the raised inscription of the plaque was next placed on the plate and the plate was placed under vacuum and exposed as before to actinic radiation for 4.5 minutes. The exposed plate was subsequently placed in a processing machine for this type of flexographic printing plate where using Cyrel® Flex Solvent (E. I. du Pont de Nemours and Company, Wilmington, DE) the unexposed, unhardened areas of the plate were washed off, in about 13 minutes, leaving behind a three dimensional pattern. A conventional mixture of sand and wax was now packed over this pattern to form upon removal of the plate a female mold into which bronze was cast to form a plaque which faithfully reproduced both the background pattern as well as the raised lettering. The plaque was finished with buffing of the raised letters and staining of the background as is customary in this trade.

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WHAT IS CLAIMED IS:

1. A process for photofabricating master relief patterns for the production of casting molds using a photohardenable, solvent soluble layer having a front and a back surface and a thickness in the range of 0.010 to 0.5 inch (0.25 to 12.7 mm), comprising the steps of:

- (1) exposing the layer through the back surface to a first imagewise modulated actinic radiation for a predetermined duration selected to penetrate the layer and render it imagewise insoluble to a first preselected depth which measured from the back surface is less than the total thickness of the photohardenable layer,
- (2) exposing the layer a second time through the back surface to unmodulated actinic radiation for a time sufficient to render insoluble the photohardenable layer to a second preselected depth which measured from the back surface is less than the first preselected depth,
- (3) exposing the layer through the front surface to a second imagewise modulated actinic radiation, for a time sufficient to render insoluble the photohardenable layer to a depth extending from the front surface to at least said second preselected depth, and
- (4) subjecting the layer to the action of a solvent to remove any portions of the layer, not rendered solvent insoluble in steps (1) through (3).

2. A process according to Claim 1 where in steps (1) and (2) are reversed.

3. A process according to Claim 1 wherein the photohardenable layer is prepared from a composition comprising a polymer of a conjugated diolefin hydrocarbon, a nongaseous ethylenically unsaturated compound and an organic, radiation-sensitive, free radical generating photoinitiator or photoinitiator system.

4. A process according to Claim 3 wherein the conjugated diolefin hydrocarbon polymer is a polymer selected from butadiene/acrylonitrile, butadiene/acrylonitrile/acrylic acid, butadiene/styrene, styrene-butadiene-styrene block copolymer and styrene-isoprene-styrene block copolymer.

5. A process according to Claim 1 wherein the solvent used in step (4) is taken from the group consisting of organic solvent, aqueous solution and mixtures thereof.

6. A process according to Claim 1 wherein the solvent used in step (4) is water.

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FIG. 1

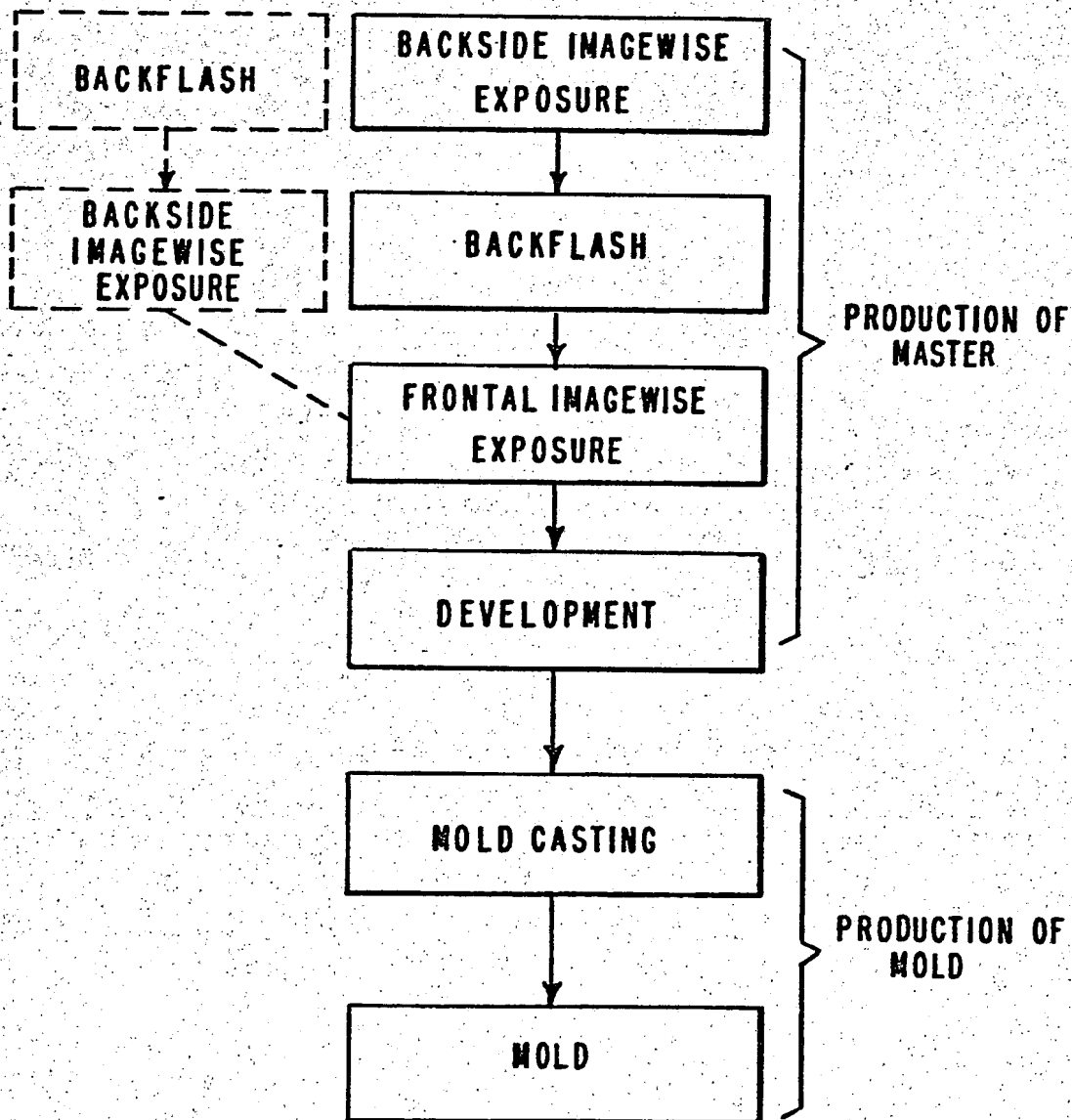


FIG. 2

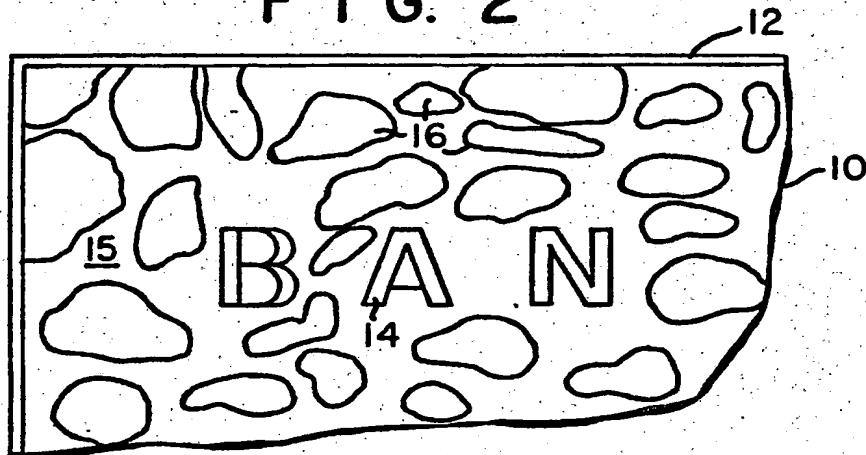


FIG. 3

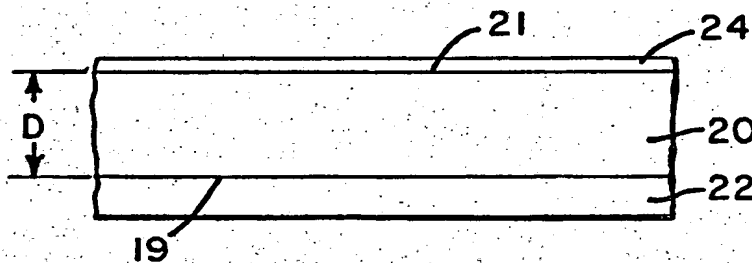


FIG. 4

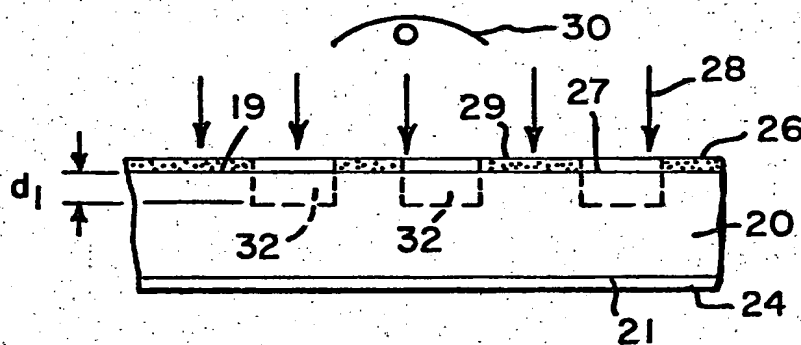


FIG. 5

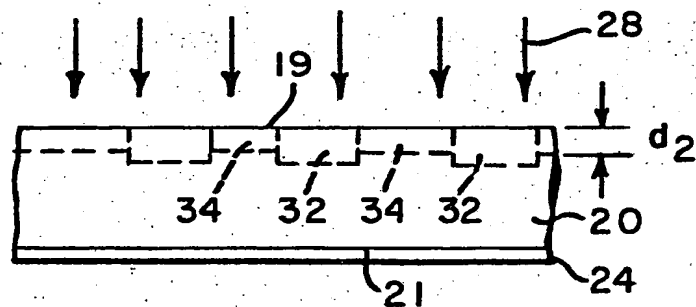


FIG. 6

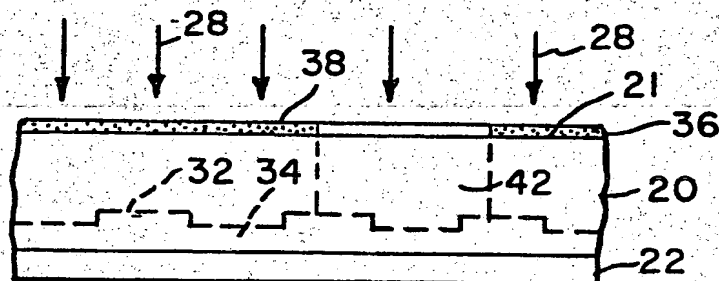


FIG. 7

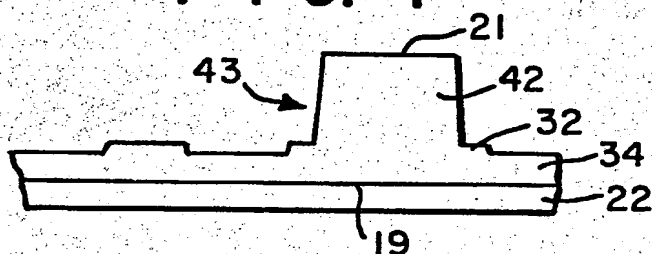


FIG. 8

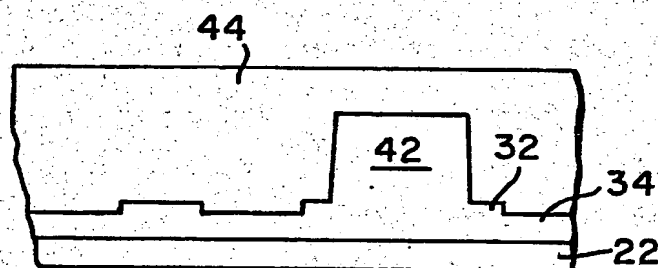
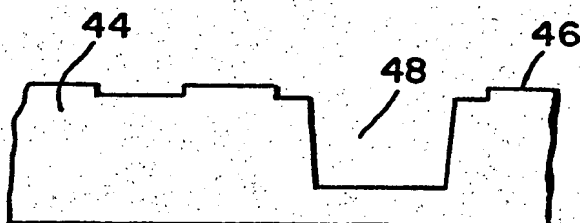


FIG. 9





Europäisches Patentamt
European Patent Office
Office européen des brevets

Publication number:

0 196 033
A3

EUROPEAN PATENT APPLICATION

Application number: 86103949.3

Int. Cl.: G 03 F 7/20, G 03 F 7/26

Date of filing: 22.03.86

Priority: 26.03.85 US 716096

Applicant: E.I. DU PONT DE NEMOURS AND COMPANY,
1007 Market Street, Wilmington Delaware 19898 (US)

Date of publication of application: 01.10.86
Bulletin 86/40

Inventor: Wojcik, Michael S., 503 Cabot Drive, Hockessin
Delaware 19707 (US)

Designated Contracting States: DE FR GB IT NL SE

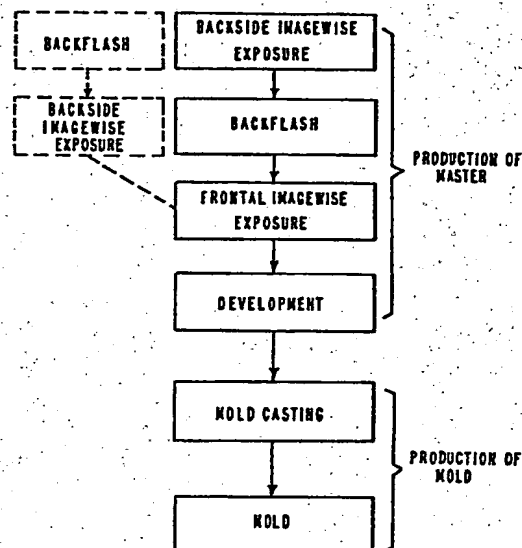
Date of deferred publication of search
report: 07.09.88 Bulletin 88/36

Representative: Werner, Hans-Karsten, Dr. et al,
Deichmannhaus am Hauptbahnhof, D-5000 Köln 1 (DE)

Multilevel imaging of photopolymer relief layer for the preparation of casting molds.

Process for photofabricating master relief patterns from photohardenable layers, e.g., 0.01 to 0.5 inch (0.25 to 12.7 mm in thickness) which comprises: (1) exposing the layer through the back surface to first imagewise modulated actinic radiation for time to render layer insoluble to first preselected depth which when measured from back surface is less than layer thickness, (2) exposing overall to actinic radiation through back to render layer insoluble to second preselected depth which when measured from back surface is less than first preselected depth, (3) exposing imagewise through front surface to actinic radiation for a time sufficient to render exposed areas of layer insoluble to depth extending from front surface to at least second preselected depth, and (4) solvent removing soluble areas of layer.

The master relief pattern is useful in making casting molds.



EP 0 196 033 A3



European Patent
Office

EUROPEAN SEARCH REPORT

0196033

Application Number

EP 86 10 3949

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 4)
X,Y	GB-A-2 035 602 (J.A. POLLAK) * Page 3, lines 41-120; claims; figures *	1-6	G 03 F 7/20 G 03 F 7/26
Y	FR-A-2 286 420 (ASAHI KASEI) * Claim; figures *	1-6	
Y	US-A-3 663 222 (KIYOSHI AKAMATSU) * Column 4, lines 44-50; claims *	1-6	
A	DE-A-2 426 610 (SUGIMORI NORIYUKI) * Figure 1. *	1-6	
A	DE-A-1 917 294 (H. BRENDEL) * Claims; page 7, lines 7-13 *	1-6	
A	DE-A-2 614 525 (ASAHI KASEI) * Figures 11-13 *	1-6	
A,D	EP-A-0 169 294 (ASAHI KASEI) * Claims *	1-6	
A	GB-A-1 304 835 (BKT DISPLAYS) * Whole document *	1	
A	DE-A- 397 983 (W.R. BUSCH) * Whole document *	1	
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 25-05-1988	Examiner RASSCHAERT A.
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference Hi-bu 001969wo	FOR FURTHER ACTION See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)	
International application No. PCT/US00/03953	International filing date (day/month/year) 16/02/2000	Priority date (day/month/year) 25/03/1999
International Patent Classification (IPC) or national classification and IPC H01J9/24		
Applicant MINNESOTA MINING AND MANUFACTURING COMPANY et al.		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.



2. This REPORT consists of a total of 7 sheets, including this cover sheet.

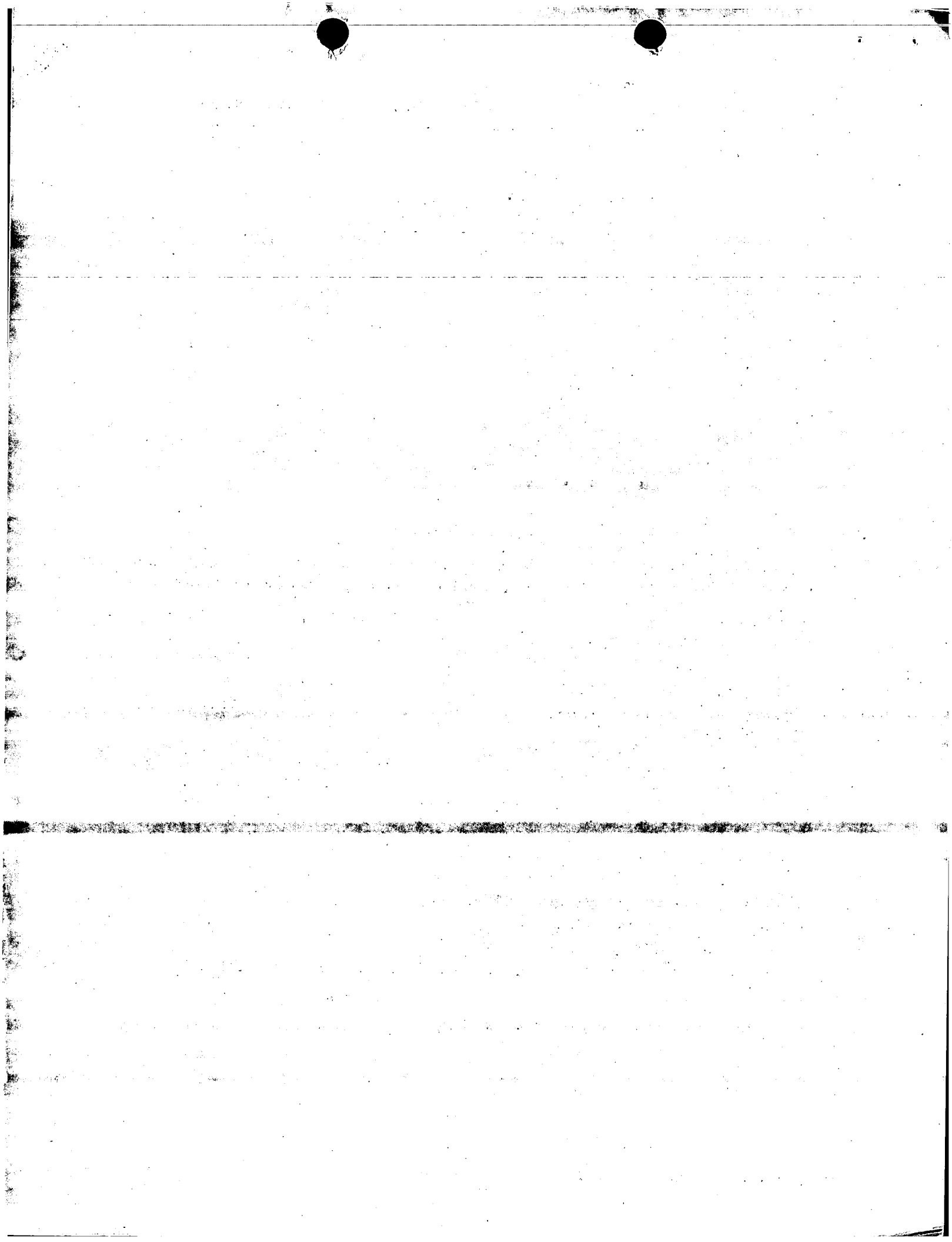
- ☒ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

These annexes consist of a total of 3 sheets.

3. This report contains indications relating to the following items:

- I ☒ Basis of the report
- II ☐ Priority
- III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- IV ☐ Lack of unity of invention
- V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI ☒ Certain documents cited
- VII ☒ Certain defects in the international application
- VIII ☒ Certain observations on the international application

Date of submission of the demand 16/08/2000	Date of completion of this report 03.07.2001
Name and mailing address of the international preliminary examining authority:  European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized officer Meul, H Telephone No. +49 89 2399 2494 



INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/US00/03953

I. Basis of the report

1. With regard to the **elements** of the international application (*Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17)*):

Description, pages:

1-10 as originally filed

Claims, No.:

1-11 as received on 03/04/2001 with letter of 02/04/2001

Drawings, sheets:

1/2,2/2 as originally filed

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

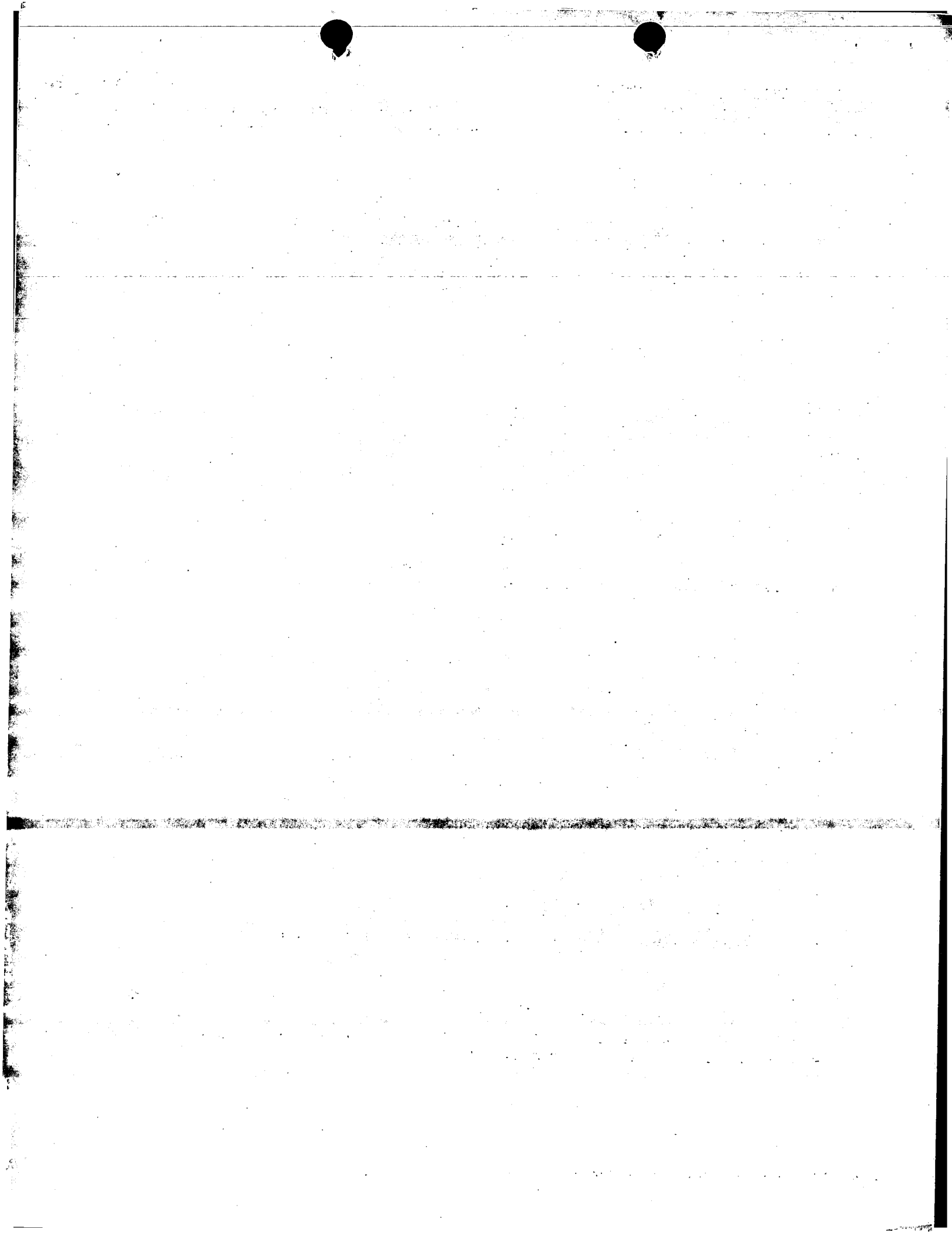
- ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
- ☐ the language of publication of the international application (under Rule 48.3(b)).
- ☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- ☐ contained in the international application in written form.
- ☐ filed together with the international application in computer readable form.
- ☐ furnished subsequently to this Authority in written form.
- ☐ furnished subsequently to this Authority in computer readable form.
- ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

- ☐ the description, pages:
- ☐ the claims, Nos.:



INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/US00/03953

☐ the drawings, sheets:

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)

6. Additional observations, if necessary:

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims	1-11
	No:	Claims	
Inventive step (IS)	Yes:	Claims	1-11
	No:	Claims	
Industrial applicability (IA)	Yes:	Claims	1-11
	No:	Claims	

2. Citations and explanations
see separate sheet

VI. Certain documents cited

1. Certain published documents (Rule 70.10)

and / or

2. Non-written disclosures (Rule 70.9)

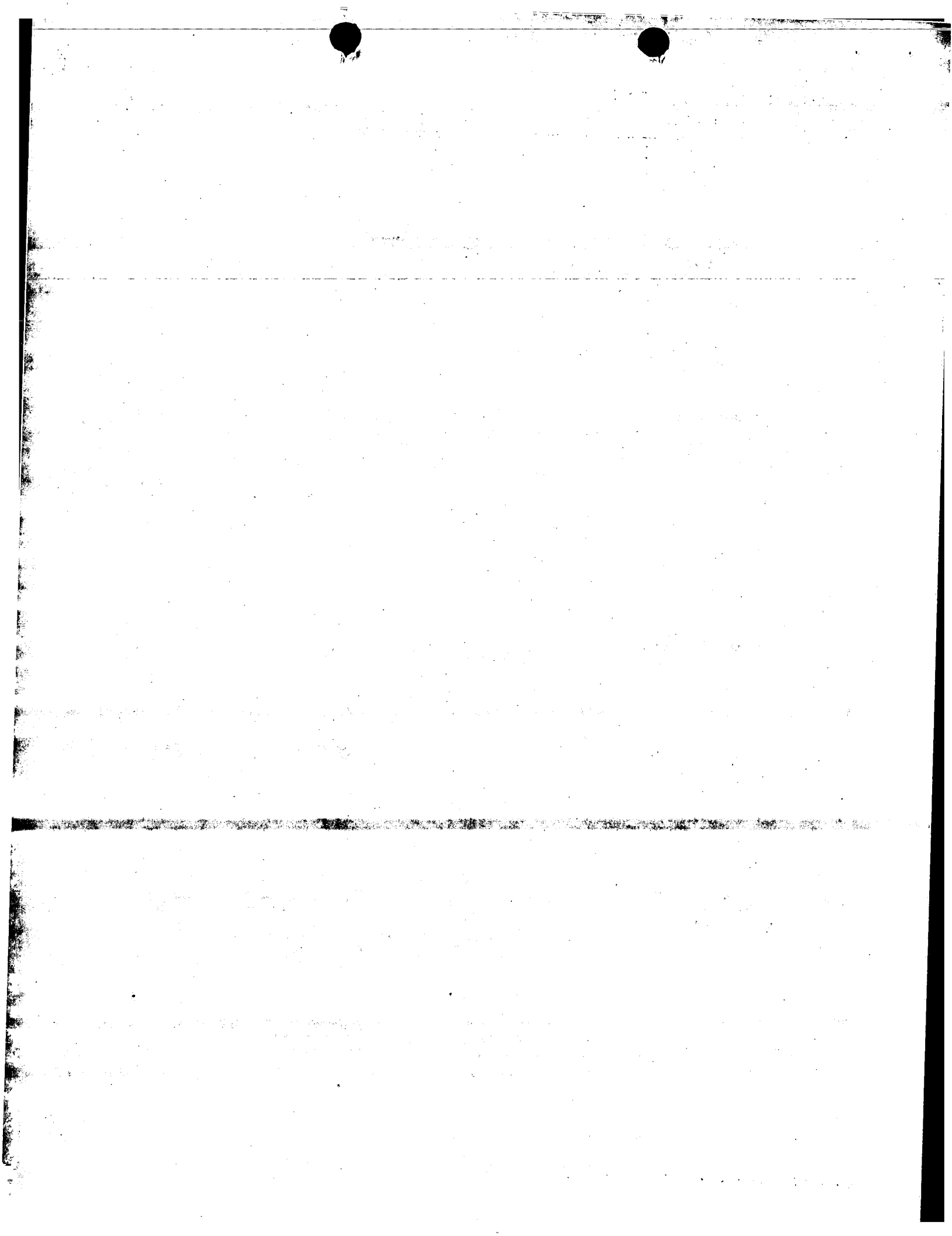
see separate sheet

VII. Certain defects in the international application

The following defects in the form or contents of the international application have been noted:
see separate sheet

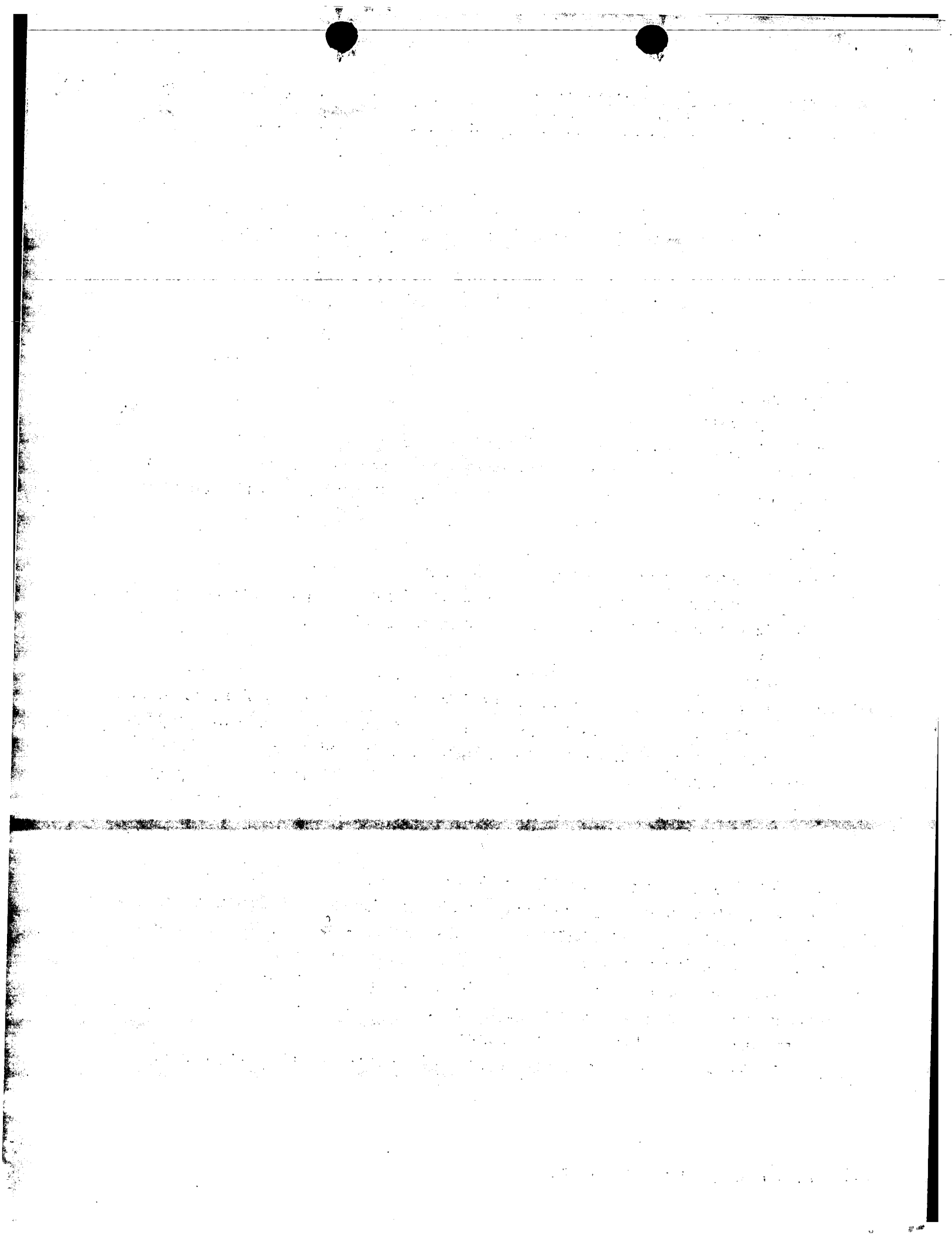
VIII. Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:
see separate sheet



**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

International application No. PCT/US00/03953



R Item V

Reasoned statement under Article 35 (2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

Technical field

The invention relates to a method of producing a substrate for a plasma display panel by providing a rib on a base and to an assembly of a mould and a rib precursor used in the method.

Closest prior art

WO 99/10909 A and corresponding EP 0 935 275 A1 (=D1) disclose a process for fabricating a plasma display panel comprising a base and a rib wherein a mould formed of silicone is filled with a barrier rib paste and contacted with a base. Subsequently, the mould is removed and the rib precursor is fired.

Problem

To provide a process and a mould for mass production of a substrate for a plasma display panel, capable of being repeatedly used without causing breakage of the base or the ribs (see p. 1, l. 21 to p. 2, l. 9 of the present description).

Solution

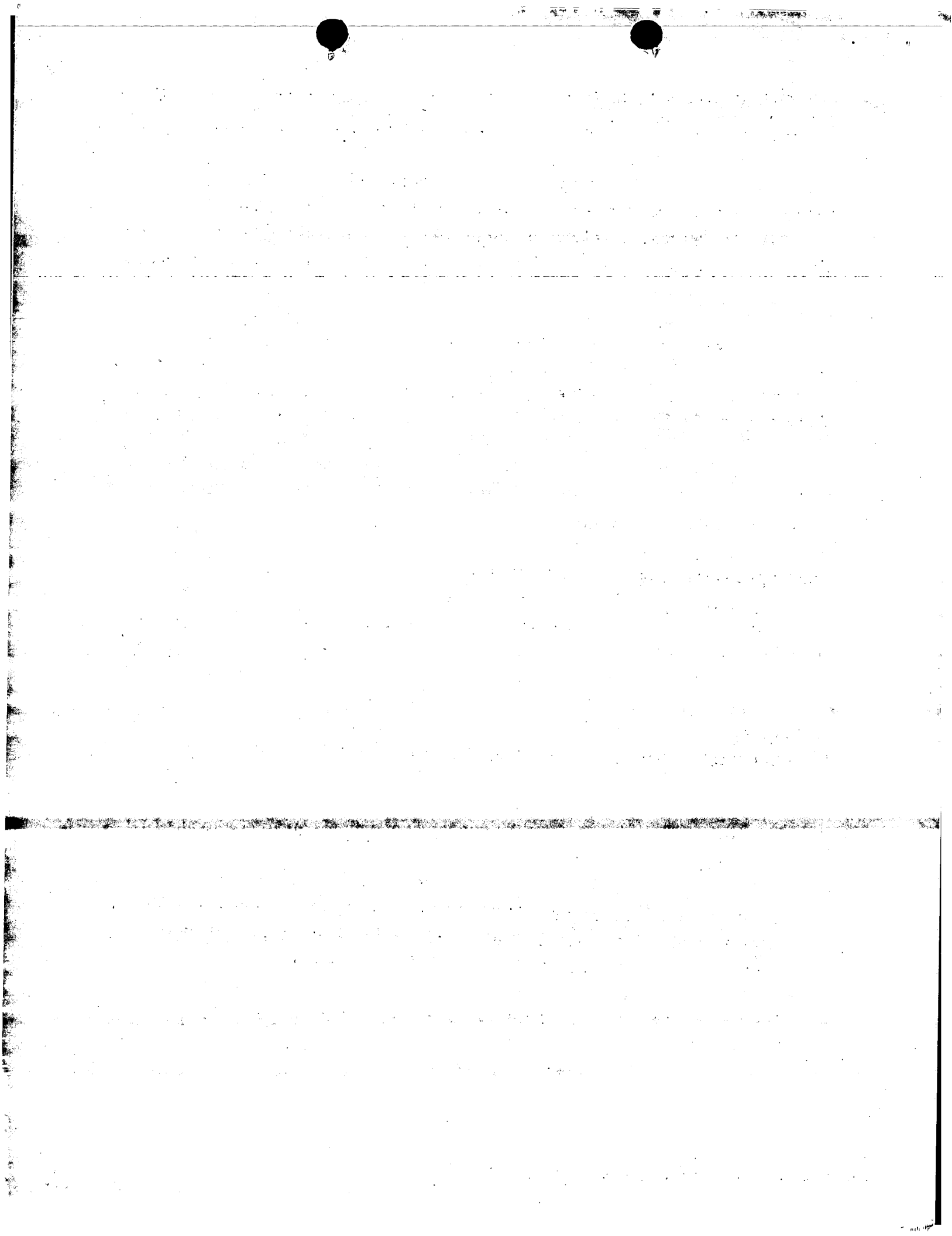
A rib precursor containing a first photo-setting initiator having a first absorption edge and a first photo-setting component is filled into a mould obtained by photo-setting of a second photo-setting initiator having a second absorption edge whose wavelength is shorter than a wavelength corresponding to said first absorption edge of said first photo-setting initiator and said rib precursor is exposed to light having a wavelength longer than a wavelength corresponding to said second absorption edge (see claims 1 and 2 for the method and claim 8 for the assembly of a mould and a rib precursor).

Assessment

None of the presently available prior art documents discloses or fairly suggests the present combination of mould and rib precursor materials. More specifically, the documents WO 99/10909 A (=D1), FR 2738393 A, and JP 09-012336 A do not teach to use a photo-setting component in the mould and/or the rib material.

The non-prepublished document WO 99/60446 A (see section VI of the present report) discloses a method of producing a substrate for a plasma display panel using a photosensitive rib paste and a plastic mould.

EP 0196033 A describes the photofabrication of master relief patterns by using a



**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT - SEPARATE SHEET**

International application No. PCT/US00/03953

material comprising a photo-setting component and a photo-setting initiator. There is no incitement to fill the master relief with another photosensitive material having an absorption edge whose wavelength is longer than a wavelength corresponding to an absorption edge of the master relief pattern and to use this assembly for fabricating a substrate for a plasma display panel.

Therefore, the subject-matter of independent claims 1, 2 and 8 is novel and involves an inventive step. Dependent claims 3-7 and 9-11 define advantageous developments of the methods of claims 1 and 2 and the assembly of claim 8, respectively, and as such also meet the requirements of the PCT with respect to novelty and inventive step.

Re Item VI

Certain documents cited

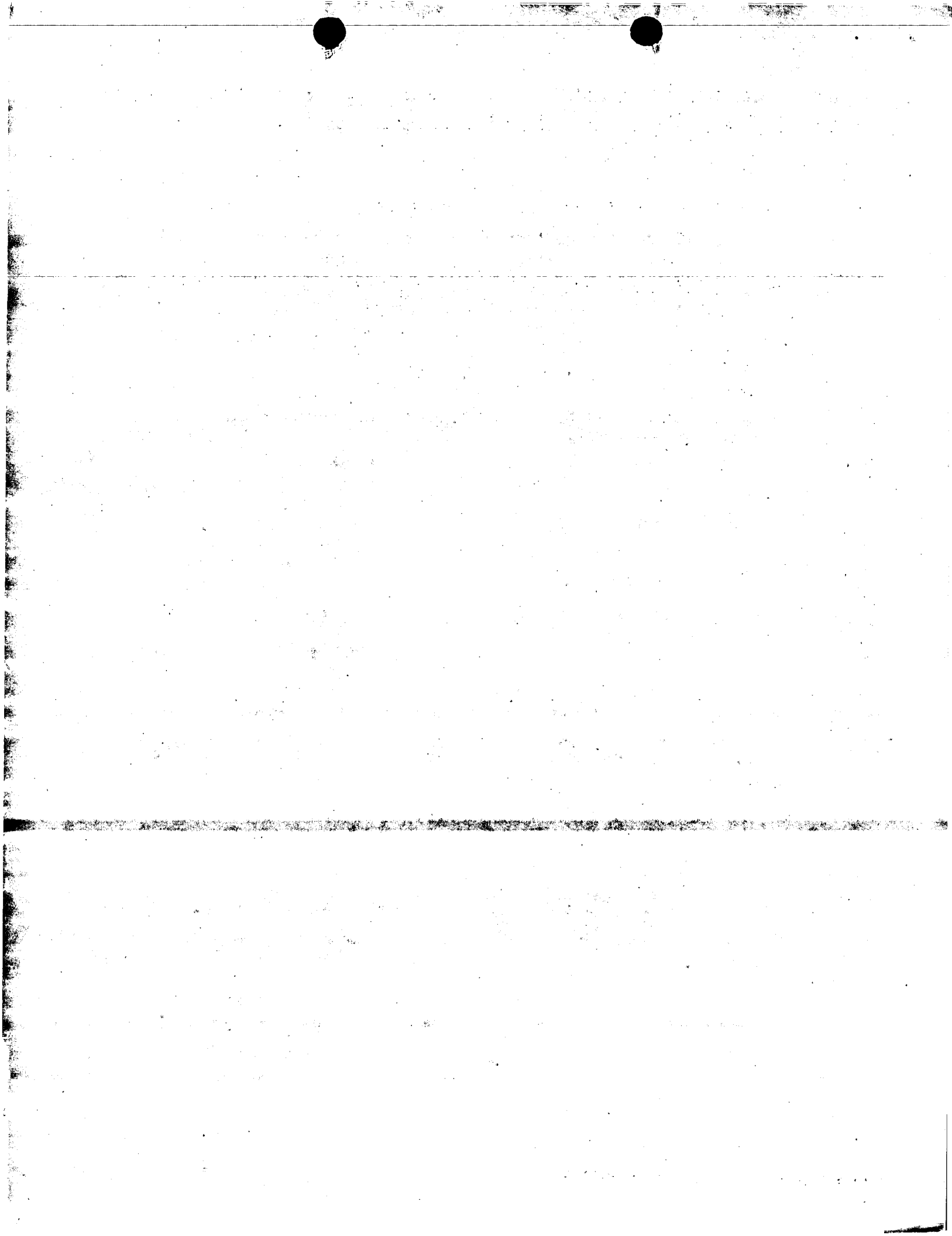
Certain published documents (Rule 70.10)

Application No Patent No	Publication date (day/month/year)	Filing date (day/month/year)	Priority date (valid claim) (day/month/year)
WO 99/60446 A1	25.11.99	05.05.99	18.05.98

Re Item VII

Certain defects in the international application

1. The unit 'cps' employed on page 6 is not additionally expressed in terms of the unit stipulated by Rule 10.1 PCT.
2. Contrary to the requirements of Rule 5.1 (a) (ii) PCT, the relevant background art disclosed in the documents D1 and D2 is not mentioned in the description, nor are these documents identified therein.
3. The description is not in conformity with the claims as required by Rule 5.1 (a) (iii) PCT.



**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT - SEPARATE SHEET**

International application No. PCT/US00/03953

Re Item VIII

Certain observations on the international application

1. A lack of clarity arises in claim 2 because there is no antecedent for 'said first absorption edge of said first photo-setting initiator' in the preceding part of the claim.

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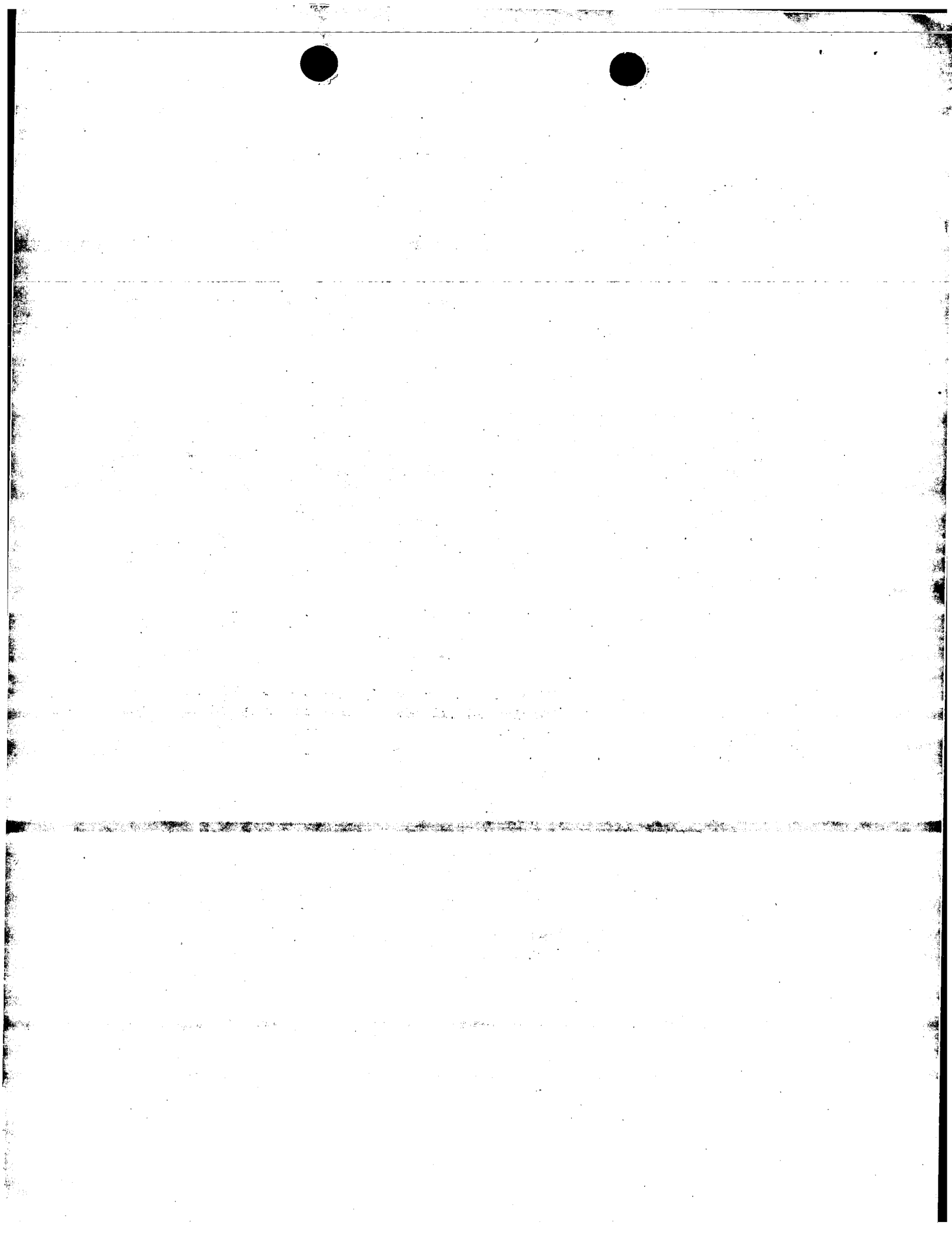
1/4

PCT REQUEST

54769PCT1A

Original (for SUBMISSION) - printed on 08.02.2000 02:01:10 PM

0	For receiving Office use only	
0-1	International Application No.	
0-2	International Filing Date	
0-3	Name of receiving Office and "PCT International Application"	
0-4	Form - PCT/RO/101 PCT Request	
0-4-1	Prepared using	PCT-EASY Version 2.90 (updated 15.12.1999)
0-5	Petition The undersigned requests that the present international application be processed according to the Patent Cooperation Treaty	
0-6	Receiving Office (specified by the applicant)	United States Patent and Trademark Office (USPTO) (RO/US)
0-7	Applicant's or agent's file reference	54769PCT1A
I	Title of invention	METHOD OF PRODUCING SUBSTRATE FOR PLASMA DISPLAY PANEL AND MOLD USED IN THE METHOD
II	Applicant	
II-1	This person is:	applicant only
II-2	Applicant for	all designated States except US
II-4	Name	MINNESOTA MINING AND MANUFACTURING COMPANY
II-5	Address:	3M Center Post Office Box 33427 Saint Paul, MN 55133-3427 United States of America
II-6	State of nationality	US
II-7	State of residence	US
II-8	Telephone No.	(651) 733-1500
II-9	Facsimile No.	(651) 736-7586
III-1	Applicant and/or inventor	
III-1-1	This person is:	applicant and inventor
III-1-2	Applicant for	US only
III-1-4	Name (LAST, First)	YOKOYAMA, Chikafumi
III-1-5	Address:	5-12-41-102, Suge Tamaku Kawasaki-shi, Kanagawa 214-0001 Japan
III-1-6	State of nationality	JP
III-1-7	State of residence	JP



PCT REQUEST

Original (for SUBMISSION) - printed on 08.02.2000 02:01:10 PM

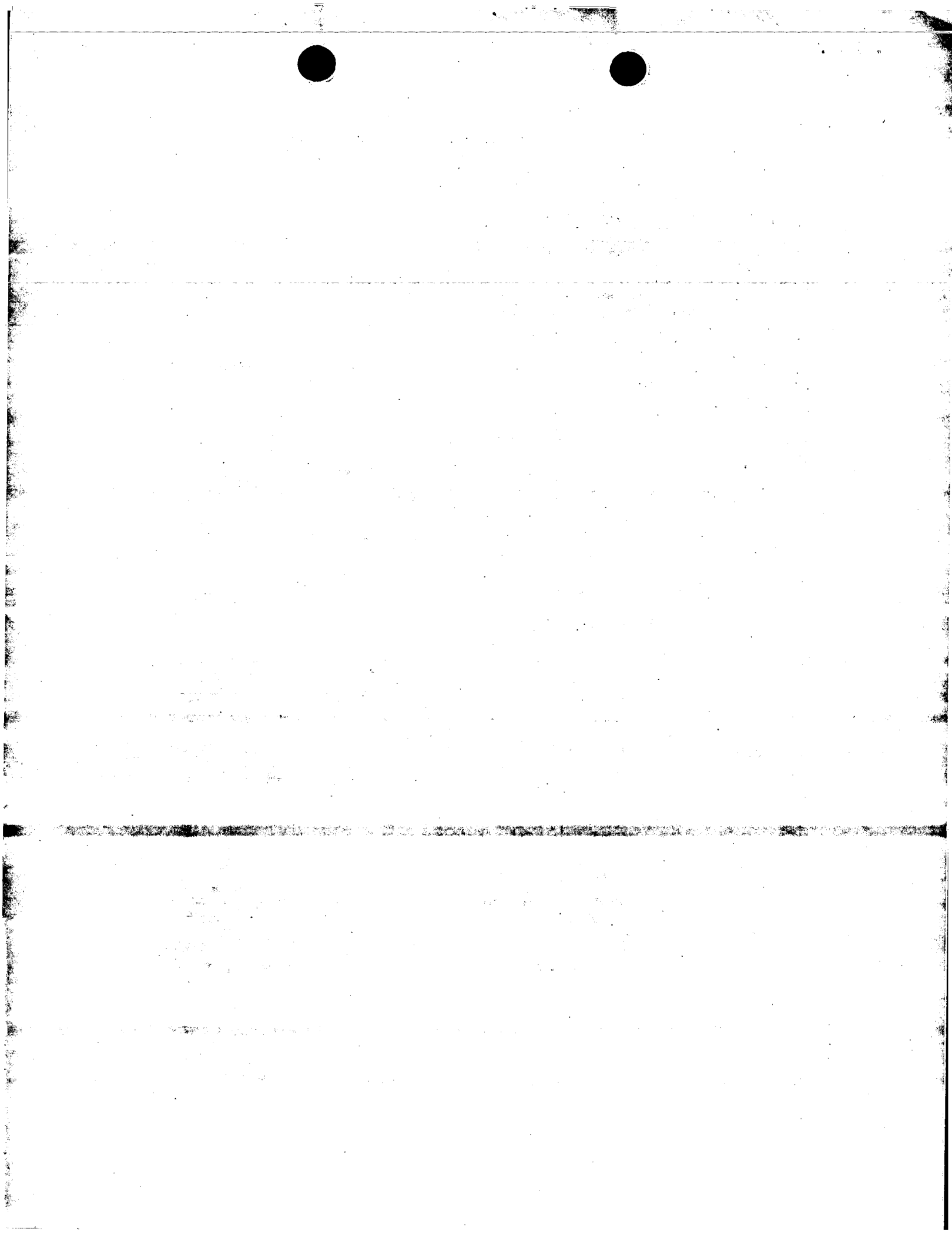
IV-1	Agent or common representative; or address for correspondence The person identified below is hereby/has been appointed to act on behalf of the applicant(s) before the competent International Authorities as:	agent
IV-1-1	Name (LAST, First)	PECHMAN, Robert J.
IV-1-2	Address:	Office of Intellectual Property Counsel Post Office Box 33427 Saint Paul, MN 55133-3427 United States of America
IV-1-3	Telephone No.	(651) 737-0631
IV-1-4	Facsimile No.	(651) 736-7586
IV-2	Additional agent(s)	additional agent(s) with same address as first named agent
IV-2-1	Name(s)	GRISWOLD, Gary L.; BATES, Carolyn A.; CHERNIVEC, Gerald F.; LITTLE, Douglas B.; SPRAGUE, Robert W.
V	Designation of States	
V-1	Regional Patent (other kinds of protection or treatment, if any, are specified between parentheses after the designation(s) concerned)	AP: GH GM KE LS MW SD SL SZ TZ UG ZW and any other State which is a Contracting State of the Harare Protocol and of the PCT EA: AM AZ BY KG KZ MD RU TJ TM and any other State which is a Contracting State of the Eurasian Patent Convention and of the PCT EP: AT BE CH&LI CY DE DK ES FI FR GB GR IE IT LU MC NL PT SE and any other State which is a Contracting State of the European Patent Convention and of the PCT OA: BF BJ CF CG CI CM GA GN GW ML MR NE SN TD TG and any other State which is a member State of OAPI and a Contracting State of the PCT
V-2	National Patent (other kinds of protection or treatment, if any, are specified between parentheses after the designation(s) concerned)	AE AL AM AT (patent and utility model) AU AZ BA BB BG BR BY CA CH&LI CN CR CU CZ (patent and utility model) DE (patent and utility model) DK (patent and utility model) DM EE (patent and utility model) ES FI (patent and utility model) GB GD GE GH GM HR HU ID IL IN IS JP KE KG KP KR (patent and utility model) KZ LC LK LR LS LU LV MA MD MG MK MN MW MX (patent and utility model) MY NL (patent and utility model) NO (patent and utility model) OM TR PT (patent and utility model) RO (patent and utility model) RU (patent and utility model) SD (patent and utility model) SE (patent and utility model) SI (patent and utility model) SK (patent and utility model) SL (patent and utility model) SM (patent and utility model) SN (patent and utility model) SR (patent and utility model) SZ (patent and utility model) TC (patent and utility model) TD (patent and utility model) TM (patent and utility model) TN (patent and utility model) TR (patent and utility model) TT TZ UA (patent and utility model) UG (patent and utility model) UZ (patent and utility model) VM (patent and utility model) YU (patent and utility model) ZW (patent and utility model)

PCT REQUEST

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V-5	Precautionary Designation Statement In addition to the designations made under items V-1, V-2 and V-3, the applicant also makes under Rule 4.9(b) all designations which would be permitted under the PCT except any designation(s) of the State(s) indicated under item V-6 below. The applicant declares that those additional designations are subject to confirmation and that any designation which is not confirmed before the expiration of 15 months from the priority date is to be regarded as withdrawn by the applicant at the expiration of that time limit.	
V-6	Exclusion(s) from precautionary designations	NONE
VI-1	Priority claim of earlier national application	
VI-1-1	Filing date	25 March 1999 (25.03.1999)
VI-1-2	Number	11-82003
VI-1-3	Country	JP
VII-1	International Searching Authority Chosen	European Patent Office (EPO) (ISA/EP)
VIII	Check list	number of sheets electronic file(s) attached
VIII-1	Request	4 -
VIII-2	Description	10 -
VIII-3	Claims	2 -
VIII-4	Abstract	1 54769pct-a-abs.txt
VIII-5	Drawings	2 -
VIII-7	TOTAL	19
VIII-8	Accompanying items	paper document(s) attached electronic file(s) attached
VIII-8	Fee calculation sheet	✓ -
VIII-16	PCT-EASY diskette	- diskette
VIII-17	Other (specified):	Transmittal Letter -
VIII-17	Other (specified):	Itemized Return Postcard -
VIII-17	Other (specified):	Certified Copy of Resolution of Board of Directors of Minnesota -
VIII-18	Figure of the drawings which should accompany the abstract	1
VIII-19	Language of filing of the international application	English
IX-1	Signature of applicant or agent	<i>Douglas B. Little</i>
IX-1-1	Name	MINNESOTA MINING AND MANUFACTURING COMPANY
IX-1-2	Name of signatory	LITTLE, Douglas B.
IX-1-3	Capacity	Assistant Chief Intellectual Property Counsel



PCT REQUEST

54769PCT1A

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10-1	Date of actual receipt of the purported international application	
10-2	Drawings:	
10-2-1	Received	
10-2-2	Not received	
10-3	Corrected date of actual receipt due to later but timely received papers or drawings completing the purported international application	
10-4	Date of timely receipt of the required corrections under PCT Article 11(2)	
10-5	International Searching Authority	ISA/EP
10-6	Transmittal of search copy delayed until search fee is paid	

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11-1	Date of receipt of the record copy by the International Bureau	
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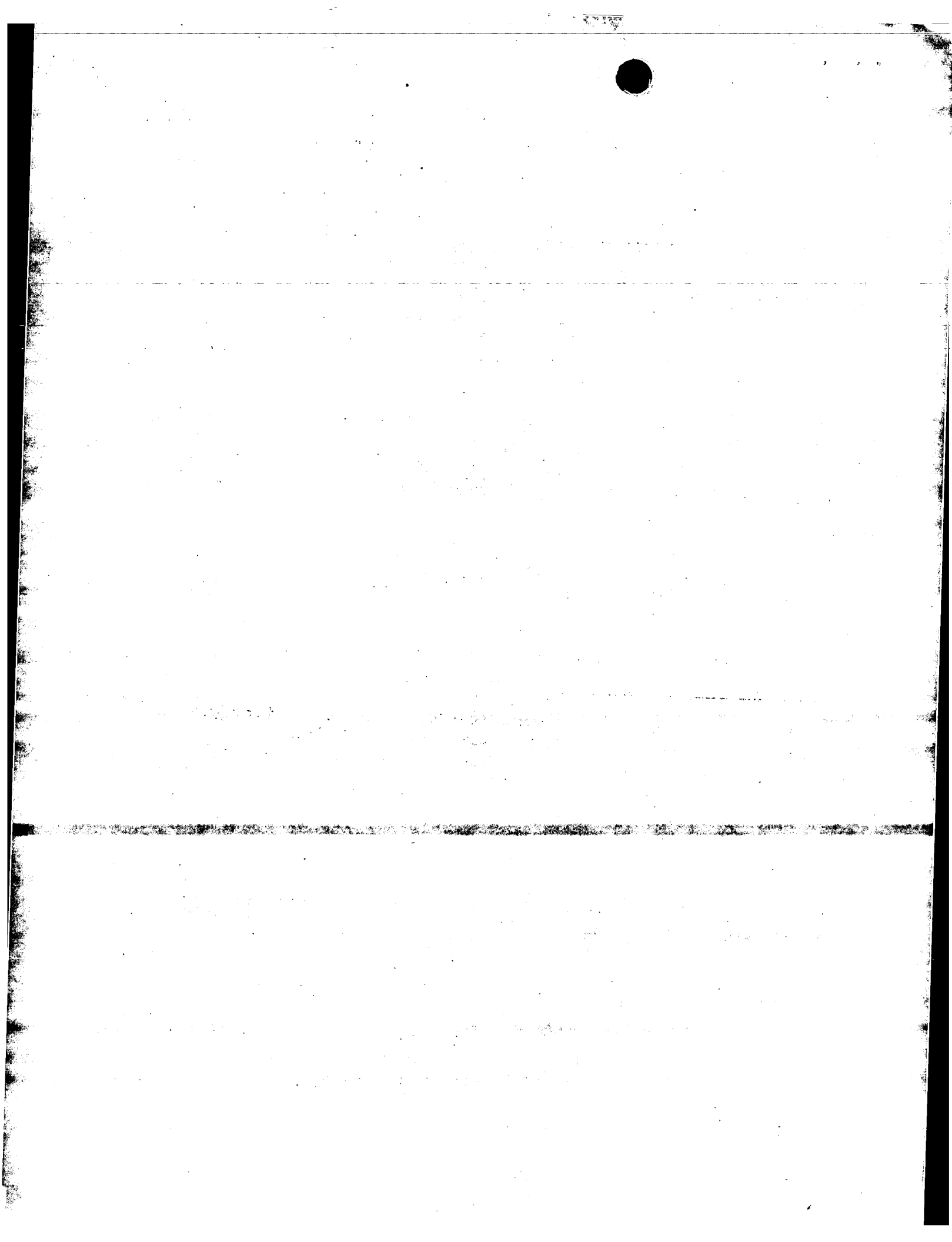
PCT (ANNEX - FEE CALCULATION SHEET)

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0	For receiving Office use only		
0-1	International Application No.		
0-2	Date stamp of the receiving Office		
0-4	Form - PCT/RO/101 (Annex)		
0-4-1	PCT Fee Calculation Sheet Prepared using	PCT-EASY Version 2.90 (updated 15.12.1999)	
0-9	Applicant's or agent's file reference	54769PCT1A	
2	Applicant	MINNESOTA MINING AND MANUFACTURING COMPANY, et al.	
12	Calculation of prescribed fees	fee amount/multiplier	total amounts (USD)
12-1	Transmittal fee T	⇒	240
12-2	Search fee S	⇒	990
12-3	International fee Basic fee (first 30 sheets) b1	427	
12-4	Remaining sheets	0	
12-5	Additional amount (X)	10	
12-6	Total additional amount b2	0	
12-7	b1 + b2 = B	427	
12-8	Designation fees Number of designations contained in international application	83	
12-9	Number of designation fees payable (maximum 8)	8	
12-10	Amount of designation fee (X)	92	
12-11	Total designation fees D	736	
12-12	PCT-EASY fee reduction R	-132	
12-13	Total International fee (B+D-R) I	⇒	1,031
12-17	TOTAL FEES PAYABLE (T+S+I+P)	⇒	2,261
12-19	Mode of payment	authorization to charge deposit account	
12-20	Deposit account instructions The receiving Office:	United States Patent and Trademark Office (USPTO) (RO/US)	
12-20-1	is hereby authorized to charge the total fees indicated above to my deposit account	✓	
12-20-2	is hereby authorized to charge any deficiency or credit any over-payment in the total fees indicated above to my deposit account	✓	
12-21	Deposit account No.	13-3723	
12-22	Date	08 February 2000 (08.02.2000)	



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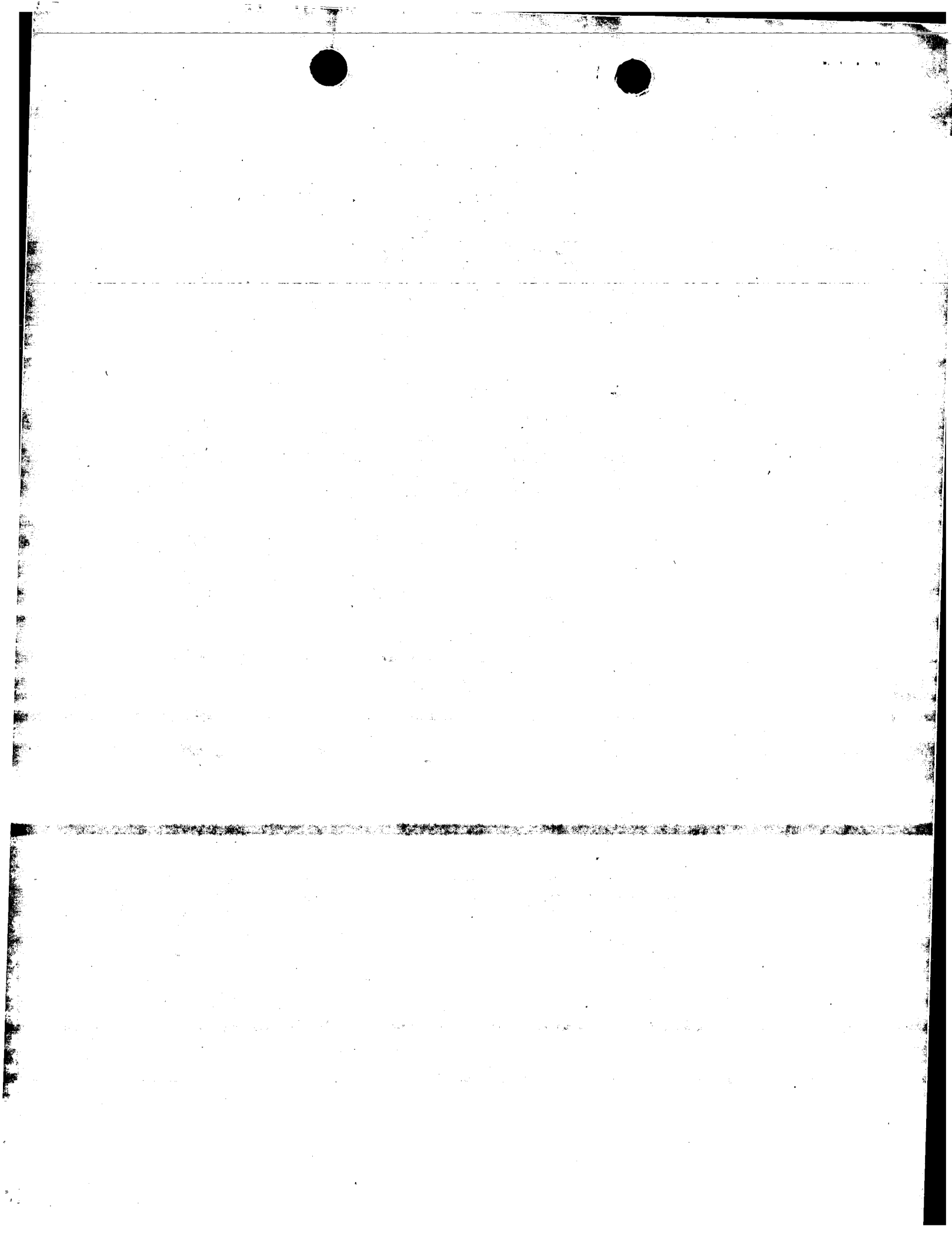
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12-23	Name and signature	Douglas B. Little, Assistant Chief Intellectual Property Counsel <i>Douglas B. Little</i>
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VALIDATION LOG AND REMARKS

13-2-3	Validation messages Names	Green? Agent 1.: Where several first/given names are indicated, they should preferably be separated by a comma. Please verify.
		Green? Agent 2.: Where several first/given names are indicated, they should preferably be separated by a comma. Please verify.
		Green? Agent 3.: Where several first/given names are indicated, they should preferably be separated by a comma. Please verify.
		Green? Agent 4.: Where several first/given names are indicated, they should preferably be separated by a comma. Please verify.
		Green? Agent 5.: Where several first/given names are indicated, they should preferably be separated by a comma. Please verify.
		Green? Agent 6.: Where several first/given names are indicated, they should preferably be separated by a comma. Please verify.
13-2-6	Validation messages Contents	Yellow! The power of attorney or a copy of the general power of attorney will need to be furnished unless all applicants sign the request form.
		Green? Priority 1. The priority document is not enclosed. (The applicant must furnish it within 16 months from the earliest priority date claimed)



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13-2-8	Validation messages Payment	Green? Please ensure that you have a valid deposit account with the receiving Office selected.
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